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20 Years'
CHAPTERWISE TOPICWISE
(2021-2002)

JEE Main
SOLVED PAPERS
Chemistry

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ARIHANT PRAKASHAN (Series), MEERUT

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PREFACE

JEE Main is a gateway examination for candidates expecting to seek admission in Bachelor in Engineering (BE), Bachelor of Technology (B.Tech) and Bachelor of Architecture (B.Arch) at Indian Institutes of Information Technology (IIITs), National Institutes of Technology (NITs), Delhi Technological University and other Centrally Funded Technical Institutes (CFTIs).

JEE Main is also an examination which is like screening examination for JEE Advanced (The gateway examination to India's most reputed Technical Institutes, Indian Institutes of Technology— IITs).

To make the students well-versed with the pattern as well as the level of the questions asked in the exam, this book contains **Chapterwise Topicwise Solutions of Questions asked in Last 20 Years' Examinations of JEE Main** (formerly known as AIEEE). Solutions to all the questions have been kept very detailed and accurate. Along with the indication of level of the exam, this book will also teach you to solve the questions objectively in the examination.

We hope this book would be highly beneficial for the students. We would be grateful if any discrepancy or mistake in the questions or answers is brought to our notice so that these could be rectified in subsequent editions.

Publisher

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SYLLABUS

SECTION- A (Physical Chemistry)

UNIT 1 Some Basic Concepts in hemistry

Matter and its nature, Dalton's atomic theory; Concept of atom, molecule, element and compound; Physical quantities and their measurements in Chemistry, precision and accuracy, significant figures, S.I. Units, dimensional analysis; Laws of chemical combination; Atomic and molecular masses, mole concept, molar mass, percentage composition, empirical and molecular formulae; Chemical equations and stoichiometry.

UNIT 2 States of Matter

Classification of matter into solid, liquid and gaseous states.

Gaseous State Measurable properties of gases; Gas laws - Boyle's law, Charle's law, Graham's law of diffusion, Avogadro's law, Dalton's law of partial pressure; Concept of Absolute scale of temperature; Ideal gas equation, Kinetic theory of gases (only postulates); Concept of average, root mean square and most probable velocities; Real gases, deviation from Ideal behaviour, compressibility factor, van der Waals'

Equation, liquefaction of gases, critical constants.

Liquid State Properties of liquids - vapour pressure, viscosity and surface tension and effect of temperature on them (qualitative treatment only).

Solid State Classification of solids: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea); Bragg's Law and its applications, Unit cell and lattices, packing in solids (fcc, bcc and hcp lattices), voids, calculations involving unit cell parameters, imperfection in solids; electrical, magnetic and dielectric properties.

UNIT 3 Atomic Structure

Discovery of sub-atomic particles (electron, proton and neutron); Thomson and Rutherford atomic models and their limitations; Nature of electromagnetic radiation, photoelectric effect; spectrum of hydrogen atom, Bohr model of hydrogen atom - its postulates, derivation of the relations for energy of the electron and radii of the different orbits, limitations of Bohr's model; dual nature of matter, de-Broglie's relationship, Heisenberg uncertainty principle.

Elementary ideas of quantum mechanics, quantum mechanical model of atom, its important features,ψ and $\psi 2$, concept of atomic orbitals as one electron wave functions; Variation of ψ and $\psi 2$ with r for 1s and 2s orbitals; various quantum numbers (principal, angular momentum and magnetic quantum numbers) and their significance; shapes of s, p and d - orbitals, electron spin and spin quantum number; rules for filling electrons in orbitals – aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of elements, extra stability of half-filled and completely filled orbitals.

UNIT 4 Chemical Bonding and Molecular Structure

Kossel Lewis approach to chemical bond formation, concept of ionic and covalent bonds.

Ionic Bonding Formation of ionic bonds, factors affecting the formation of ionic bonds; calculation of lattice enthalpy.

Covalent Bonding Concept of electronegativity, Fajan's rule, dipole moment; Valence Shell Electron Pair Repulsion (VSEPR) theory and shapes of simple molecules.

Quantum mechanical approach to covalent bonding Valence bond theory - Its important features, concept of **hybridization** involving s, p and d orbitals; Resonance.

Molecular Orbital Theory Its important features, LCAOs, types of molecular orbitals (bonding, antibonding), sigma and pi-bonds, molecular orbital electronic configurations of homonuclear diatomic molecules, concept of bond order, bond length and bond energy.

Elementary idea of metallic bonding. Hydrogen bonding and its applications.

UNIT 5 Chemical Thermodynamics

Fundamentals of thermodynamics System and surroundings, extensive and intensive properties, state functions, types of processes.

First law of thermodynamics Concept of work, heat internal energy and enthalpy, heat capacity, molar heat capacity, Hess's law of constant heat summation; Enthalpies of bond dissociation, combustion, formation, atomization, sublimation, phase transition, hydration, ionization and solution.

Second law of thermodynamics Spontaneity of processes; ΔS of the universe and ΔG of the system as criteria for spontaneity, ΔG° (Standard Gibb's energy change) and equilibrium constant.

UNIT 6 Solutions

Different methods for expressing concentration of solution - molality, molarity, mole fraction, percentage (by volume and mass both), vapour pressure of solutions and Raoult's Law - Ideal and non-ideal solutions, vapour pressure - composition plots for ideal and non-ideal solutions.

Colligative properties of dilute solutions - relative lowering of vapour pressure, depression of freezing point, elevation of boiling point and osmotic pressure; Determination of molecular mass using colligative properties; Abnormal value of molar mass, van't Hoff factor and its significance.

UNIT 7 Equilibrium

Meaning of equilibrium, concept of dynamic equilibrium.

Equilibria involving physical processes Solid -liquid, liquid - gas and solid - gas equilibria, Henry's law, general characteristics of equilibrium involving physical processes.

Equilibria involving chemical processes Law of chemical equilibrium, equilibrium constants (K and K) and their significance, significance of ΔG and ΔG° in chemical equilibria, factors affecting equilibrium concentration, pressure, temperature, effect of catalyst; Le -Chatelier's principle.

Ionic equilibrium Weak and strong electrolytes, ionization of electrolytes, various concepts of acids and bases (Arrhenius, Bronsted - Lowry and Lewis) and their ionization, acid-base equilibria (including multistage ionization) and ionization constants, ionization of water, pH scale, common ion effect, hydrolysis of salts and pH of their solutions, solubility of sparingly soluble salts and solubility products, buffer solutions.

UNIT 8 Redox Reactions and Electrochemistry

Electronic concepts of oxidation and reduction, redox reactions, oxidation number, rules for assigning oxidation **number,** balancing of redox reactions.

Eectrolytic and metallic conduction,
conductance in electrolytic solutions, specific and molar conductivities and their variation with concentration: Kohlrausch's **law and its applications.**

Electrochemical cells - Electrolytic and Galvanic cells, different types of electrodes, electrode potentials including standard electrode potential, half - cell and cell reactions, emf of a Galvanic cell and its measurement; Nernst equation and its applications; Relationship between cell potential and Gibbs' energy change; Dry cell and lead accumulator; Fuel cells; Corrosion and its prevention.

UNIT 9 Chemical Kinetics

Rate of a chemical reaction, factors affecting the rate of reactions concentration, temperature, pressure and catalyst; elementary and complex reactions, order and molecularity of reactions, rate law, rate constant and its units, differential and integral forms of zero and first order reactions, their characteristics and half - lives, effect of temperature on rate of reactions - Arrhenius theory, activation energy and its calculation, collision theory of bimolecular gaseous reactions (no derivation).

UNIT 10 Surface Chemistry

Adsorption Physisorption and chemisorption and their characteristics, factors affecting adsorption of gases on solids- Freundlich and Langmuir adsorption isotherms, adsorption from solutions.

Catalysis Homogeneous and heterogeneous, activity and selectivity of solid catalysts, enzyme catalysis and its mechanism.

Colloidal state distinction among true solutions, colloids and suspensions, classification of colloids - lyophilic, lyophobic; multi molecular, macromole-cular and associated colloids (micelles), preparation and properties of colloids Tyndall effect, Brownian movement, electrophoresis, dialysis, coagulation and flocculation; Emulsions and their characteristics.

SECTION- B (Inorganic Chemistry)

UNIT 11 Classification of Elements and Periodicity in Properties

Periodic Law and Present Form of the Periodic Table, *s, p, d* and *f* Block Elements, Periodic Trends in Properties of Elementsatomic and Ionic Radii, Ionization Enthalpy, Electron Gain Enthalpy, Valence, Oxidation States and Chemical Reactivity.

UNIT 12 General Principles and Processes of Isolation of Metals

Modes of occurrence of elements in nature, minerals, ores; steps involved in the extraction of metals - concentration, reduction (chemical and electrolytic methods) and refining with special reference to the extraction of Al, Cu, Zn and Fe; Thermodynamic and electrochemical principles involved in the extraction of metals.

UNIT 13 Hydrogen

Position of hydrogen in periodic table, isotopes, preparation, properties and uses of hydrogen; physical and chemical properties of water and heavy water; Structure, preparation, reactions and uses of hydrogen peroxide; Classification of hydrides ionic, covalent and interstitial; Hydrogen as a fuel.

UNIT 14 *s* - Block Elements

(Alkali and Alkaline Earth Metals)

Group 1 and 2 Elements

General introduction, electronic configuration and general trends in physical and chemical properties of elements, anomalous properties of the first element of each group, diagonal relationships.

Preparation and properties of some important compounds - sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogen carbonate; Industrial uses of lime, limestone, Plaster of Paris and cement; Biological significance of Na, K, Mg and Ca.

UNIT 15 *p* - Block Elements

Group 13 to Group 18 Elements, General Introduction Electronic configuration and general trends in physical and chemical properties of elements across the periods and down the groups; unique behaviour of the first element in each group.

Group wise study of the *p* – block elements

Group 13 Preparation, properties and uses of boron and aluminium; structure, properties and uses of borax, boric acid, diborane, boron trifluoride, aluminium chloride and alums.

Group 14 Tendency for catenation; Structure, properties and uses of allotropes and oxides of carbon, silicon tetrachloride, silicates, zeolites and silicones.

Group 15 Properties and uses of nitrogen and phosphorus; Allotrophic forms of phosphorus; Preparation, properties, structure and uses of ammonia nitric acid, phosphine and phosphorus halides,(PCl_3, PCl_5); Structures of oxides and oxoacids of nitrogen and phosphorus.

Group 16 Preparation, properties, structures and uses of dioxygen and ozone; Allotropic forms of sulphur; Preparation, properties, structures and uses of sulphur dioxide, sulphuric acid (including its industrial preparation); Structures of oxoacids of sulphur.

Group 17 Preparation, properties and uses of chlorine and hydrochloric acid; Trends in the acidic nature of hydrogen halides; Structures of Interhalogen compounds and oxides and oxoacids of halogens.

Group 18 Occurrence and uses of noble gases; Structures of fluorides and oxides of xenon.

UNIT 16 *d* – and *f* – Block Elements

Transition Elements General introduction, electronic configuration, occurrence and characteristics, general trends in properties of the first row transition elements - physical properties, ionization enthalpy, oxidation states,

atomic radii, colour, catalytic behaviour, magnetic properties, complex formation, interstitial compounds, alloy formation; Preparation, properties and uses of $K_2Cr_2O_7$ and $KMnO_4$.

Inner Transition Elements Lanthanoids Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction. Actinoids Electronic configuration and oxidation states.

UNIT 17 Coordination Compounds

Introduction to coordination compounds, Werner's theory; ligands, coordination number, denticity, chelation; IUPAC nomenclature of mononuclear coordination compounds, isomerism; Bonding Valence bond approach and basic ideas of Crystal field theory, colour and magnetic properties; importance of coordination compounds (in qualitative analysis, extraction of metals and in biological systems).

Unit 18 Environmental Chemistry

Environmental pollution Atmospheric, water and soil.

Atmospheric pollution Tropospheric and stratospheric.

Tropospheric pollutants : Gaseous pollutants Oxides of carbon, nitrogen and sulphur, hydrocarbons; their sources, harmful effects and prevention; Green house effect and Global warming; Acid rain;

Particulate pollutants Smoke, dust, smog, fumes, mist; their sources, harmful effects and prevention.

Stratospheric pollution Formation and breakdown of ozone, depletion of ozone layer - its mechanism and effects.

Water pollution Major pollutants such as, pathogens, organic wastes and chemical pollutants their harmful effects and prevention. Soil pollution Major pollutants such as: Pesticides (insecticides, herbicides and fungicides), their harmful effects and prevention. Strategies to control environmental pollution.

SECTION- C (Organic Chemistry)

UNIT 19 Purification & Characterisation of Organic Compounds

Purification Crystallization, sublimation, distillation, differential extraction and chromatography principles and their applications.

Qualitative analysis Detection of nitrogen, sulphur, phosphorus and halogens.

Quantitative analysis (basic principles only) Estimation of carbon, hydrogen, nitrogen, halogens, sulphur, phosphorus. Calculations of empirical formulae and molecular formulae; Numerical problems in organic quantitative analysis.

UNIT 20 Some Basic Principles of Organic Chemistry

Tetravalency of carbon; Shapes of simple molecules hybridization (*s* and *p*); Classification of organic compounds based on functional groups: —C=C—,—C=C— and those containing halogens, oxygen, nitrogen and sulphur, Homologous series; Isomerism - structural and stereoisomerism.

Nomenclature (Trivial and IUPAC)

Covalent bond fission Homolytic and heterolytic free radicals, carbocations and carbanions; stability of carbocations and free radicals, electrophiles and nucleophiles.

Electronic displacement in a covalent bond Inductive effect, electromeric effect, resonance and hyperconjugation.

Common types of organic reactions Substitution, addition, elimination and rearrangement.

UNIT 21 Hydrocarbons

Classification, isomerism, IUPAC nomenclature, general methods of preparation, properties and reactions.

Alkanes Conformations: Sawhorse and Newman projections (of ethane); Mechanism of halogenation of alkanes.

Alkenes Geometrical isomerism; Mechanism of electrophilic addition: addition of hydrogen, halogens, water, hydrogen halides (Markownikoff's and peroxide effect); Ozonolysis, oxidation, and polymerization.

Alkynes acidic character; addition of hydrogen, halogens, water and hydrogen halides; polymerization.

Aromatic hydrocarbons Nomenclature, benzene structure and aromaticity; Mechanism of electrophilic substitution: halogenation, nitration, Friedel – Craft's alkylation and acylation, directive influence of functional group in mono-substituted benzene.

UNIT 22 Organic Compounds Containing Halogens

General methods of preparation, properties and reactions; Nature of C—X bond; Mechanisms of substitution reactions. Uses/environmental effects of chloroform, iodoform

UNIT 23 Organic Compounds Containing Oxygen

General methods of preparation, properties, reactions and uses.

Alcohols, Phenols and Ethers

Alcohols Identification of primary, secondary and tertiary alcohols; mechanism of dehydration.

Phenols Acidic nature, electrophilic substitution reactions: halogenation, nitration and sulphonation, Reimer - Tiemann reaction.

Ethers Structure.

Aldehyde and Ketones Nature of carbonyl group;

Nucleophilic addition to >C=O group, relative reactivities of aldehydes and ketones; Important reactions such as - Nucleophilic addition reactions (addition of HCN, NH_3 and its derivatives), Grignard reagent; oxidation; reduction (Wolff Kishner and Clemmensen) acidity of α-hydrogen, aldol condensation, Cannizzaro reaction, Haloform reaction; Chemical tests to distinguish between aldehydes and Ketones. Carboxylic Acids Acidic strength and factors affecting it.

UNIT 24 Organic Compounds Containing Nitrogen

General methods of preparation, properties, reactions and uses.

Amines Nomenclature, classification, structure basic character and identification of primary, secondary and tertiary amines and their basic character.

Diazonium Salts Importance in synthetic organic chemistry.

UNIT 25 Polymers

General introduction and classification of polymers, general methods of polymerization-addition and condensation, copolymerization; Natural and synthetic rubber and vulcanization; some important polymers with emphasis on their monomers and uses - polythene, nylon, polyester and bakelite.

UNIT 26 Biomolecules

General introduction and importance of biomolecules.

Carbohydrates Classification: aldoses and ketoses; monosaccharides (glucose and fructose), constituent monosaccharides of oligosacchorides (sucrose, lactose, maltose) and polysaccharides (starch, cellulose, glycogen).

Proteins Elementary Idea of α-amino acids, peptide bond, . polypeptides; proteins: primary, secondary, tertiary and quaternary structure (qualitative idea only), denaturation of proteins, enzymes.

Vitamins Classification and functions.

Nucleic Acids Chemical constitution of DNA and RNA. Biological functions of Nucleic acids.

UNIT 27 Chemistry in Everyday Life

Chemicals in medicines Analgesics, tranquilizers, antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamins - their meaning and common examples.

Chemicals in food Preservatives, artificial sweetening agents - common examples.

Cleansing agents Soaps and detergents, cleansing action.

UNIT 28 Principles Related to Practical Chemistry

- Detection of extra elements (N, S, halogens) in organic compounds; Detection of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl and amino groups in organic compounds.
- Chemistry involved in the preparation of the following
- Inorganic compounds Mohr's salt, potash alum.
- Organic compounds Acetanilide,
  p-nitroacetan ilide, aniline yellow, iodoform.
- Chemistry involved in the titrimetric excercises - Acids bases and the use of indicators, oxali acid vs $KMnO_4$, Mohr's salt vs $KMnO_4$.
- Chemical principles involved in the qualitative salt analysis
- Cations — Pb^{2+} , Cu^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+} NH^{4+}. Anions – CO_3^{2-}, S^{2-}, SO_4^{2-}, NO_2, NO_3, Cl^-, Br^-, I^- (Insoluble salts excluded).
- Chemical principles involved in the following experiments

1. Enthalpy of solution of $CuSO_4$
2. Enthalpy of neutralization of strong acid and strong base.
3. Preparation of lyophilic and lyophobic sols.
4. Kinetic study of reaction of iodide ion with hydrogen peroxide at room temperature.

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01

Some Basic Concepts in Chemistry

TOPIC 1

Nature of Matter, Significant Figures and Laws of Chemical Combinations

01 The number of significant figures in 0.00340 is ..... .

[2021, 25 July Shift-II]

Ans. ***(3)***

Number of significant figures = 0.00340

$= 3.40 \times 10^{-3}$

So, total number of significant figure = 3.

Here,

None-zero digits and trailing zero are counted.

(Note You can convert it into simplest form first.)

02 The number of significant figures in 50000.020×10^{-3} is ..... .

[2021, 26 Feb Shift-I]

Ans. ***(7)***

Non-zero digits are always significant. Any zeros between two significant digits are significant.

∴ Zero's between 5 and 2 are all significant.

$\underbrace{50000.020}_{\uparrow} \times 10^{-3}$

(Number of significant figures = 7)

03 Among the following statements, that which was not proposed by Dalton was **[2020, 7 Jan Shift-I]**

(a) chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

(b) when gases combine or reproduced in a chemical reaction they do so in a simple ratio by volume provided all gases are at the same T and *P*.

(c) all the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.

(d) matter consists of indivisible atoms.

Ans. ***(b)***

The postulates given in options (a), (c) and (d) are proposed by Dalton.

Option (b) is defining the Gay-Lussac's law of combining volumes of gases.

04 0.27 g of a long chain fatty acid was dissolved in 100 cm^3 of hexane. 10 mL of this solution was added dropwise to the surface of water in a round watch glass. Hexane evaporates and a monolayer is formed. The distance from edge to centre of the watch glass is 10 cm. What is the height of the monolayer?

[Density of fatty acid = 0.9 g cm^{-3}; $\pi = 3$] **[2019, 8 April Shift-II]**

(a) 10^{-6} m (b) 10^{-4} m

(c) 10^{-8} m (d) 10^{-2} m

Ans. ***(a)***

100 mL (cm^3) of hexane contains 0.27 g of fatty acid.

In 10 mL solution, mass of the fatty acid,

$$m = \frac{0.27}{100} \times 10$$

$$= 0.027 \text{ g}$$

Density of fatty acid, $d = 0.9 \text{ g cm}^{-3}$

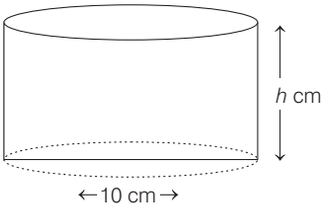
∴ Volume of the fatty acid over the watch glass,

$$V = \frac{m}{d} = \frac{0.027}{0.9}$$

$$= 0.03 \text{ cm}^3$$

Let, height of the cylindrical monolayer = *h* cm

∵ Volume of the cylinder = Volume of fatty acid



$$\Rightarrow \quad V = \pi r^2 \times h$$

$$\Rightarrow \quad h = \frac{V}{\pi r^2}$$

$$= \frac{0.03 \text{ cm}^3}{3 \times (10)^2 \text{ cm}^2}$$

$$= 1 \times 10^{-4} \text{ cm}$$

$$= 1 \times 10^{-6} \text{ m}$$

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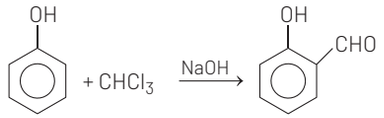
TOPIC 2

Atomic Mass, Molecular Mass and Formulae of Compounds

05 A solution of phenol in chloroform when treated with aqueous NaOH gives compound *P* as a major product. The mass percentage of carbon in *P* is ..... .
(to the nearest integer)
(Atomic mass: C = 12; H = 1; O = 16)
[2020, 6 Sep Shift-II]

Ans. ***(69)***

A solution of phenol in chloroform react with aqueous NaOH gives compound *P* (salicylaldehyde).



(*P*)
(Salicylaldehyde)

$\therefore$ Mass % of C in *P*(Compound)

$$= \frac{\text{Mass of C}}{\text{Mass of Compound}} \times 100$$

$$\begin{cases} \text{Here, mass of C} = 12 \times 7 \\ \text{mass of compound (P)} = \underset{(12\times 7+}{\text{C}}\ \underset{6\times 1+}{\text{H}}\ \underset{16+2)}{\text{O}} \end{cases}$$

$$= \frac{12\times 7}{84+6+32} \times 100 = 68.85\% = 69\%$$

06 The average molar mass of chlorine is 35.5 g mol^{-1}. The ratio of ^{35}Cl to ^{37}Cl in naturally occurring chlorine is close to
[2020, 6 Sep Shift-II]

(a) 4 : 1 (b) 3 : 1
(c) 2 : 1 (d) 1 : 1

Ans. ***(b)***

Given,

Average molar mass of chlorine is 35.5 g mol^{-1}.

Naturally occurring chlorine are

	^{35}Cl	^{37}Cl
Molar ratio	x	$1-x$

Total molar ratio $= x + 1 - x = 1$

Mass average $= 35 \times x + 37 \times (1-x)$

$$35.5 = 35x + 37 - 37x$$

$$2x = 37 - 35.5;\ x = \frac{1.5}{2} = 0.75 = \frac{3}{4}$$

For ^{35}Cl, $x = \frac{3}{4}$

For ^{37}Cl; $1 - \frac{3}{4}$

$$^{35}Cl\ :\ ^{37}Cl$$

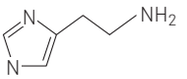
$$\frac{3}{4}\ :\ \left(1-\frac{3}{4}\right) \Rightarrow \frac{3}{4}\ :\ \frac{1}{4}$$

On simplify this ratio, we get 3 : 1.

07 The mass percentage of nitrogen in histamine is .....
[2020, 9 Jan Shift-I]

Ans. ***(37.84)***

Histamine :



Molecular formula = $C_5H_9N_3$. Molecular mass = 111

Number of nitrogen atoms per molecule = 3

Mass due to N = $3 \times 14 = 42$

$$\%\ \text{of N} = \frac{42}{111} \times 100 = 37.84\%$$

The value have a range from 37.80 to 38.20.

08 5 moles of AB_2 weight 125×10^{-3} kg and 10 moles of A_2B_2 weight 300×10^{-3} kg. The molar mass of $A(M_A)$ and molar mass of $B(M_B)$ in kg mol^{-1} are **[2019, 12 April Shift-I]**

(a) $M_A = 10 \times 10^{-3}$ and $M_B = 5 \times 10^{-3}$
(b) $M_A = 50 \times 10^{-3}$ and $M_B = 25 \times 10^{-3}$
(c) $M_A = 25 \times 10^{-3}$ and $M_B = 50 \times 10^{-3}$
(d) $M_A = 5 \times 10^{-3}$ and $M_B = 10 \times 10^{-3}$

Ans. ***(d)***

Key Idea To find the mass of *A* and *B* in the given question, mole concept is used.

$$\text{Number of moles}\,(n) = \frac{\text{given mass}\,(w)}{\text{molecular mass}\,(M)}$$

Compound	Mass of *A* (*g*)	Mass of *B* (*g*)
AB_2	M_A	$2M_B$
A_2B_2	$2M_A$	$2M_B$

We know that,

Number of moles

$$(n) = \frac{\text{given mass}\,(w)}{\text{molecular mass}\,(M)}$$

$$n \times M = w \qquad \ldots(A)$$

Using equation (A), it can be concluded that

$$5(M_A + 2M_B) = 125 \times 10^{-3}\ \text{kg} \qquad \ldots(i)$$

$$10(2M_A + 2M_B) = 300 \times 10^{-3}\ \text{kg} \qquad \ldots(ii)$$

From equation (i) and (ii)

$$\frac{1}{2}\frac{(M_A + 2M_B)}{(2M_A + 2M_B)} = \left(\frac{125}{300}\right)$$

On solving the equation, we obtain

$$M_A = 5 \times 10^{-3}\ \text{and}\ M_B = 10 \times 10^{-3}$$

So, the molar mass of $A(M_A)$ is 5×10^{-3} kg mol^{-1} and $B(M_B)$ is 10×10^{-3} kg mol^{-1}.

09 The ratio of mass per cent of C and H of an organic compound ($C_xH_yO_z$) is 6 : 1. If one molecule of the above compound ($C_xH_yO_z$) contains half as much oxygen as required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O. The empirical formula of compound $C_xH_yO_z$ is **[JEE Main 2018]**

(a) $C_3H_6O_3$ (b) C_2H_4O
(c) $C_3H_4O_2$ (d) $C_2H_4O_3$

Ans. ***(d)***

We can calculate the simplest whole number ratio of C and H from the data given, as

Element	Relative mass	Molar mass	Relative mole	Simplest whole no. ratio
C	6	12	$\frac{6}{12} = 0.5$	$\frac{0.5}{0.5} = 1$
H	1	1	$\frac{1}{1} = 1$	$\frac{1}{0.5} = 2$

Alternatively this ratio can also be calculated directly in the terms of *x* and *y* as

$$\frac{12x}{y} = \frac{6}{1}$$

(given and molar mass of C = 12, H = 1)

Now, after calculating this ratio look for condition 2 given in the question i.e. quantity of oxygen is half of the quantity required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O. We can calculate number of oxygen atoms from this as consider the equation.

$$C_xCH_y + \left[x + \frac{y}{4}\right] O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

Number of oxygen atoms required

$$= 2 \times \left[x + \frac{y}{4}\right] = \left[2x + \frac{y}{2}\right]$$

Now given, $z = \frac{1}{2}\left[2x + \frac{y}{2}\right] = \left[x + \frac{y}{4}\right]$

Here we consider *x* and *y* as simplest ratios for C and H so now putting the values of *x* and *y* in the above equation.

$$z = \left[x + \frac{y}{4}\right] = \left[1 + \frac{2}{4}\right] = 1.5$$

Thus, the simplest ratio figures for *x*, *y* and *z* are $x = 1$, $y = 2$ and $z = 1.5$

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Now, put these values in the formula given i.e.

$$C_xH_yO_z = C_1H_2O_{1.5}$$

So, empirical formula will be

$$[C_1H_2O_{1.5}] \times 2 = C_2H_4O_3$$

10 The most abundant elements by mass in the body of a healthy human adult are Oxygen (61.4%); Carbon (22.9%), Hydrogen (10.0 %); and Nitrogen (2.6%). The weight which a 75 kg person would gain if all ^1H atoms are replaced by ^2H atoms is **[JEE Main 2017]**

(a) 15 kg (b) 37.5 kg
(c) 7.5 kg (d) 10 kg

Ans. ***(c)***

Given, abundance of elements by mass oxygen = 61.4%, carbon = 22.9%, hydrogen = 10% and nitrogen = 2.6%

Total weight of person = 75 kg

$$\text{Mass due to } ^1H = \frac{75 \times 10}{100} = 7.5 \text{ kg}$$

^1H atoms are replaced by ^2H atoms,

$$\text{Mass due to } ^2H = (7.5 \times 2) \text{ kg}$$

∴ Mass gain by person = 7.5 kg

11 At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O_2 by volume for complete combustion. After combustion, the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is **[JEE Main 2016]**

(a) C_3H_8 (b) C_4H_8
(c) C_4H_{10} (d) C_3H_6

Ans. ***(None)***

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \longrightarrow \underset{75\text{ mL}}{xCO_2(g)} + \underset{30\text{mL}}{\frac{y}{2}H_2O(l)}$$

O_2 used = 20% of 375 = 75 mL

Inert part of air = 80% of 375 = 300 mL

Total volume of gases = CO_2 + Inert part of air

$$= 30 + 300 = 330 \text{ mL}$$

$$\frac{x}{1} = \frac{30}{15} \Rightarrow x = 2 \Rightarrow \frac{x + \frac{y}{4}}{1} = \frac{75}{15}$$

$$\Rightarrow \quad x + \frac{y}{4} = 5$$

$$\Rightarrow \quad x = 2,\ y = 12 \Rightarrow C_2H_{12}$$

12 A gaseous hydrocarbon gives upon combustion, 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is **[JEE Main 2013]**

(a) C_2H_4 (b) C_3H_4 (c) C_6H_5 (d) C_7H_8

Ans. ***(d)***

18 g H_2O contain 2g H.

∴ 0.72 g H_2O contain 0.08 g H 44 g CO_2 contain 12 g C.

∴ 3.08 g CO_2 contain 0.84 g C.

$$\therefore \quad C : H = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08 = 7 : 8$$

∴ Empirical formula = C_7H_8

13 The mass of potassium dichromate crystals required to oxidise 750 cm^3 of 0.6 M Mohr's salt solution is (molar mass = 392) **[AIEEE 2011]**

(a) 0.49 g (b) 0.45 g
(c) 22.05 g (d) 2.2 g

Ans. ***(c)***

Mohr's salt is $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

Only oxidisable part Fe^{2+} is

$$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Millimoles of $Fe^{2+} = 750 \times 0.6 = 450$

$$\text{Moles of } Fe^{2+} = \frac{450}{1000} = 0.450 \text{ mol}$$

$$6 \text{ mol } Fe^{2+} \equiv 1 \text{ mol } Cr_2O_7^{2-}$$

$$\therefore \quad 0.450 \text{ mol } Fe^{2+} \equiv \frac{0.450}{6}$$

$$= 0.075 \text{ mol } Cr_2O_7^{2-}$$

$$= 0.075 \times 294 \text{ g} = 22.05 \text{ g}$$

14 If we consider that 1/6, in place of 1/12, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of a substance will **[AIEEE 2005]**

(a) be a function of the molecular mass of the substance
(b) remain unchanged
(c) increase two fold
(d) decrease twice

Ans. ***(b)***

The mass of one mole of *a* substance will remain unchanged.

15 In an organic compound of molar mass 108 g mol^{-1} C, H and N atoms are present in 9 : 1 : 3.5 by weight. Molecular formula can be **[AIEEE 2002]**

(a) $C_6H_8N_2$ (b) $C_7H_{10}N$
(c) $C_5H_6N_3$ (d) $C_4H_{18}N_3$

Ans. ***(a)***

Molar mass 108 g mol^{-1}

Total part by weight = 9 + 1 + 3.5 = 13.5

$$\text{Weight of carbon} = \frac{9}{13.5} \times 108 = 72 \text{ g}$$

$$\text{Number of carbon atoms} = \frac{72}{12} = 6$$

$$\text{Weight of hydrogen} = \frac{1}{13.5} \times 108 = 8 \text{ g}$$

$$\text{Number of hydrogen atoms} = \frac{8}{1} = 8$$

$$\text{Weight of nitrogen} = \frac{3.5}{13.5} \times 108 = 28 \text{ g}$$

$$\text{Number of nitrogen atom} = \frac{28}{14} = 2$$

Hence, molecular formula = $C_6H_8N_2$.

16 Experimentally, it was found that a metal oxide has formula $M_{0.98}O$. Metal *M*, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be **[JEE Main 2013]**

(a) 7.01% (b) 4.08%
(c) 6.05% (d) 5.08%

Ans. ***(b)***

$M_{0.98}O$

Consider one mole of the oxide.

Moles of $M = 0.98$ mole of $O^{2-} = 1$

Let moles of $M^{3+} = x$

⇒ Moles of $M^{2+} = 0.98 - x$

⇒ On balancing charge,

$$(0.98 - x) \times 2 + 3x - 2 = 0$$

$$\Rightarrow \quad 1.96 - 2x + 3x - 2 = 0$$

$$\Rightarrow \quad x = 0.04$$

$$\Rightarrow \text{ Percentage of } M^{3+} = \frac{0.04}{0.98} \times 100$$

$$= 4.08\%$$

TOPIC 3

Mole Concept and Concentration Terms

17 The number of atoms in 8 g of sodium is $x \times 10^{23}$. The value of *x* is ..... .

(Nearest integer)

[Given : $N_A = 6.02 \times 10^{23}$ mol^{-1}

Atomic mass of Na = 23.0 u]

[2021, 1 Sep Shift-II]

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Ans. *(2)*

Given, mass of Na = 8g

Molar mass of Na = 23 gmol^{-1}

$$= \frac{\text{Weight of sodium atom}}{\text{Molecular mass of sodium atom}}$$

$$= \frac{\text{Number of atoms}}{\text{Avogadro's number}}$$

$$\frac{8\text{ g}}{23\text{ g}} = \frac{\text{Number of atoms}}{6.022\times10^{23}}$$

$$\text{Number of atoms} = \frac{8\times6.022}{23}\times10^{23}$$

$$\text{Number of atoms} = 2.09\times10^{23}$$

$$x \approx 2$$

Hence, answer is 2.

18 10.0 mL of 0.05 M $KMnO_4$ solution was consumed in a titration with 10.0 mL of given oxalic acid dihydrate solution. The strength of given oxalic acid solution is ..... $\times10^{-2}$ g/L.

(Round off to the nearest integer)

[2021, 27 July Shift-II]

Ans. *(1575)*

For titration of $KMnO_4$ with oxalic acid,

$$n_{eq}(KMnO_4) = n_{eq}(H_2C_2O_4\cdot2H_2O)$$

or $$\frac{10\times0.05}{1000}\times5 = \frac{10\times M}{1000}\times2$$

$$\Rightarrow \quad M = 0.125\text{ M}$$

Molar mass of $H_2C_2O_4\cdot2H_2O$

$$= 2\times1+2\times12+4\times16+2(18)$$

$$= 126\text{ g/mol}$$

Strength of oxalic acid = (126×0.125) g/L

$$= 15.75\text{ g/L}$$

$$= 1575\times10^{-2}\text{ g/L}$$

19 When 10 mL of an aqueous solution of Fe^{2+} ions was titrated in the presence of dil. H_2SO_4 using diphenylamine indicator, 15 mL of 0.02 M solution of $K_2Cr_2O_7$ was required to get the end point. The molarity of the solution containing Fe^{2+} ions is $x\times10^{-2}$ M. The value of x is ..... . (Nearest integer)

[2021, 25 July Shift-I]

Ans. *(18)*

For the given reaction,

$$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$$

Volume of aqueous solution of Fe^{2+} ion $(V_1) = 10$ mL.

Volume of $K_2Cr_2O_7$ solution $(V_2) = 15$ mL

Molarity of $K_2Cr_2O_7$, $M_2 = 0.02$ M

Milliequivalent of Fe^{2+}

= Milliequivalent of $K_2Cr_2O_7$

$$n_1M_1V_1 = n_2M_2V_2$$

$$M_1\times10\times1 = 6\times0.02\times15$$

$$\Rightarrow \quad M_1 = \frac{6\times0.02\times15}{10} = 0.18$$

$$M_1 \simeq 18\times10^{-2}\text{ M}$$

So, value of x is 18.

20 If the concentration of glucose $(C_6H_{12}O_6)$ in blood is 0.72 gL^{-1}, the molarity of glucose in blood is ..... $\times10^{-3}$ M. (Nearest integer)

[Given : Atomic mass of C = 12, H = 1, O = 16 u] **[2021, 22 July Shift-II]**

Ans. *(4)*

Molar mass of glucose $(C_6H_{12}O_6)$

$$= 12\times6+12\times1+16\times6 = 180\text{ g mol}^{-1}$$

Concentration of glucose

$$= 0.72\text{ g L}^{-1} \qquad \text{(given)}$$

$\therefore$ Molarity (M)

$$= \frac{\text{Concentration of glucose}}{\text{Molar mass of glucose}} = \frac{W_B}{M_B}$$

$$M = \frac{0.72}{180} = 0.004$$

$$= 4\times10^{-3}\text{ M}.$$

21 15 mL of aqueous solution of Fe^{2+} in acidic medium completely reacted with 20 mL of 0.03 M aqueous $Cr_2O_7^{2-}$. The molarity of the Fe^{2+} solution is ..... $\times10^{-2}$ M (Round off to the nearest integer).

[2021, 17 March Shift-I]

Ans. *(24)*

$$\overset{+6}{Cr_2O_7^{2-}} + \overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{+3}{Fe^{3+}}$$

Dichromate $(Cr_2O_7^{2-})$ oxidised Fe^{2+} to Fe^{3+} and itself get reduced to Cr^{3+}.

Valency factor of $Cr_2O_7^{2-} = 6$ as Cr gets reduced from +6 to +3.

Valency factor of $Fe^{2+} = 1$ as it gets oxidised from +2 to +3.

From law of equivalence,

Milliequivalent of $Cr_2O_7^{2-}$ = Milliequivalent of Fe^{2+}

$$M_1V_1n_1 = M_2V_2n_2$$

$$(M_1\times V_1)\times6 = (M_2\times V_2)\times1$$

$$(0.03\times20)\times6 = (M_2\times15)\,1$$

$$\Rightarrow \quad M_2 = 0.24\text{ molar}$$

$$= 24\times10^{-2}\text{ molar}$$

22 The mole fraction of a solute in a 100 molal aqueous solution ..... $\times10^{-2}$ (Round off to the nearest integer).

[Given, atomic masses H : 1.0 u, O : 16.0 u] **[2021, 17 March Shift-I]**

Ans. *(64)*

Given, molality = 100

$\Rightarrow$ 100 moles of solute in 1 kg of solvent

Mole fraction of solute (χ_{Solute})

$$= \frac{\text{Moles of solute}}{\text{Total moles}} = \frac{n_{Solute}}{n_{Solute}+n_{Solvent}}$$

$$n_{Solvent} = \frac{1000}{18} = 55.5$$

$$\chi_{Solute} = \frac{100}{100+55.5} = \frac{100}{155.5} = 0.643$$

$$\chi_{Solute} = 64.3\times10^{-2} = 64\times10^{-2}$$

23 The $NaNO_3$ weighed out to make 50 mL of an aqueous solution containing 70.0 mg Na^+ per mL is ..... g. (Rounded off to the nearest integer)

[Given : Atomic weight in g mol^{-1}, Na : 23 ; N : 14 ; O : 16].

[2021, 26 Feb Shift-II]

Ans. *(13)*

70 mg Na^+ is present in 1 mL of $NaNO_3$ solution.

$\therefore$ 50 mL of $NaNO_3$ will contain

$$= 70\times50\text{ mg}$$

$$= \frac{70\times50}{1000} = 3.5\text{ gm}$$

Moles of Na^+ in solution = Moles of $NaNO_3$ in solution

$$[\because NaNO_3 \longrightarrow Na^+ + NO_3^-]$$

$$= \frac{3.5}{23}\text{ mol}$$

$$[\because \text{Molar mass of } Na^+ = 23\text{g mol}^{-1}]$$

Mass of $NaNO_3$ = mole × molar mass

$$[\because \text{molar mass of } NaNO_3 = 85\text{ gmol}^{-1}]$$

$$= \frac{3.5}{23}\times85 = 12.934\text{ g} \simeq 13\text{ g}$$

24 The mole fraction of glucose $(C_6H_{12}O_6)$ in an aqueous binary solution is 0.1. The mass percentage of water in it, to the nearest integer, is ..... .

[2020, 3 Sep Shift-I]

Ans. *(47.00)*

Let, for glucose :

Mass = w_B g, mole = n_B

and mole fraction = χ_B

(Molar mass, $M_B = 180$ g mol^{-1})

For water : mass = w_A g,

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mole = n_A and mole fraction = χ_A

(Molar mass, $M_A = 18\ g\ mol^{-1}$)

Where, $\chi_A + \chi_B = 1$

$$\Rightarrow \quad \frac{\chi_B}{\chi_A} = \frac{\chi_B}{1-\chi_B} = \frac{0.1}{0.9} = \frac{1}{9}$$

$$\Rightarrow \quad \frac{\frac{n_B}{n_A + n_B}}{\frac{n_A}{n_A + n_B}} = \frac{1}{9}$$

$$\Rightarrow \quad \frac{n_B}{n_A} = \frac{1}{9} \Rightarrow \frac{\frac{w_B}{180}}{\frac{w_A}{18}} = \frac{1}{9} \Rightarrow \frac{w_B}{180} \times \frac{18}{w_A} = \frac{1}{9}$$

$$\Rightarrow \quad \frac{w_B}{w_A} = \frac{10}{9} \Rightarrow \frac{w_B}{w_A} + 1 = \frac{10}{9} + 1$$

$$\Rightarrow \quad \frac{w_A}{w_A + w_B} = \frac{9}{19}$$

$$\Rightarrow \frac{w_A}{w_A + w_B}\% = \frac{9}{19} \times 100 = 47.368 \simeq 47.00$$

So, mass percentage of water (*A*) in the solution is 47.00.

25 6.023×10^{22} molecules are present in 10 g of a substance '*x*'. The molarity of a solution containing 5 g of substance '*x*' in 2 L solution is ..... $\times 10^{-3}$. **[2020, 3 Sep Shift-II]**

Ans. ***(25)***

Given, 6.023×10^{23} molecules are present in 10 g substance.

Number of moles

$$= \frac{\text{Number of molecules}}{6 \times 10^{23}} = \frac{\text{Mass (given)}}{\text{Molar mass}}$$

$$\text{Molar mass} = \frac{10 \times 6.023 \times 10^{23}}{6.023 \times 10^{22}}$$

$$= 100\ \text{g/mol}$$

We know that

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution } (l)}$$

$$\left[\begin{matrix}\text{Given, molarity of solution containing} = 5 \\ \text{of subtance, Volume } = 2\text{L}\end{matrix}\right]$$

$$= \frac{(5/100)}{2} = \frac{5}{100 \times 2}$$

$$= 0.025 = 25 \times 10^{-3}$$

26 The strengths of 5.6 volume hydrogen peroxide (of density 1 g/mL) in terms of mass percentage and molarity (*M*), respectively, are

(Take molar mass of hydrogen peroxide as 34 g/mol)

[2020, 3 Sep Shift-II]

(a) 0.85 and 0.25 (b) 0.85 and 0.5

(c) 1.7 and 0.5 (d) 1.7 and 0.25

Ans. ***(c)***

Volume of hydrogen = 5.6

Volume strength = 11.2 × molarity

$$\Rightarrow \quad \text{Molarity} = \frac{\text{Volume strength}}{11.2}$$

$$= \frac{5.6}{11.2} = 0.5$$

Suppose, that the solution taken is = 1 L

Mass of solution = 1000 mL × 1 g/mL

= 1000 g

Mass of solute = Moles × Molar mass

$$= 0.5 \times 34$$

$$[\because \text{molar mass of } H_2O_2 = 34]$$

$$= 17\ \text{g}$$

$$\Rightarrow \quad \text{Mass \%} = \frac{17}{1000} \times 100 = 1.7\%$$

27 A 100 mL solution was made by adding 1.43 g of $Na_2CO_3 \cdot xH_2O$. The normality of the solution is 0.1 N. The value of *x* is ..... . **[2020, 4 Sep Shift-II]**

Ans. ***(10)***

Molar mass of $Na_2CO_3 \cdot xH_2O$.

(Atomic mass of Na = 23, C = 12, O = 16)

$$= 23 \times 2 + 12 + 48 + 18x$$

$$= 46 + 12 + 48 + 18x =$$

$(106 + 18x)$

Equivalent weight of $Na_2CO_3 \cdot xH_2O$

$$= \frac{\text{Molar mass}}{n\ \text{factor}} = \frac{M}{2} = (53 + 9x)$$

[Here, *m* = molar mass and *n* factor = 2]

$$\text{Gram equivalent} = \frac{\text{Weight}}{\text{Equivalent weight}}$$

[Given, weight of $Na_2CO_3 \cdot xH_2O = 1.43$ g]

Hence, gram equivalent of

$$Na_2CO_3 \cdot xH_2O = \frac{1.43}{53 + 9x}$$

$$\text{Normality} = \frac{G_{meq}}{V_{litre}};\ 0.1 = \frac{\frac{1.43}{53 + 9x}}{0.1}$$

{As, volume = 100 mL = 0.1 L

So, $\quad 10^{-2} = \frac{1.43}{53 + 9x} \Rightarrow 53 + 9x = 143$

$$9x = 90 \Rightarrow x = 10.00$$

28 Ferrous sulphate heptahydrate is used to fortify foods with iron. The amount (in grams) of the salt required to achieve 10 ppm of iron in 100 kg of wheat is ..... .

Atomic weight : Fe = 55.85; S = 32.00; O = 16.00

[2020, 8 Jan Shift-I]

Ans. ***(4.97)***

Ferrous sulphate heptahydrate $FeSO_4 \cdot 7H_2O$.

If the amount of the salt is '*x*' gram.

Mass of iron contained in it

$$= \frac{x \times \text{atomic mass of Fe } (= 55.85)}{\text{Molar mass of } FeSO_4 \cdot 7H_2O (= 277.85)}$$

$$= \frac{55.85x}{277.85}$$

10 ppm of iron in 100 kg of wheat, can be acheived as,

$$= \frac{\text{mass of iron} \times 10^6}{\text{mass of wheat } (= 100\ \text{kg} = 10^5\ \text{g})} = 10$$

$$= \frac{55.85x \times 10^6}{277.85 \times 10^5} = 10 \Rightarrow x = \frac{277.85}{55.85} = 4.97\ \text{g}$$

This value may vary from 4.95 to 4.99.

29 The molarity of HNO_3 in a sample which has density 1.4 g/mL and mass percentage of 63% is ..... (Molecular weight of HNO_3 = 63) **[2020, 9 Jan Shift-I]**

Ans. ***(14.00)***

For 100 g sample of the solution, mass of HNO_3 = 63 g,

$$\therefore \quad n_{HNO_3} = \frac{63}{63} = 1\ \text{mol}$$

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{100\ \text{g}}{1.4\ \text{g/mL}}$$

$$= \frac{100}{1.4}\ \text{mL} = \frac{1}{14}\ \text{L}$$

$$\text{Molarity} = \frac{n}{V(\text{L})} = \frac{1}{(1/14)} = 14\ \text{M}$$

30 A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 mL of CO_2 at $T = 298.15$ K and $p = 1$ bar. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet? [Molar mass of $NaHCO_3$ = 84 g mol^{-1}] **[2019, 11 Jan Shift-I]**

(a) 8.4 (b) 0.84 (c) 16.8 (d) 33.6

Ans. ***(a)***

$$\underset{2\ \text{mol}}{2NaHCO_3} + \underset{1\ \text{mol}}{H_2C_2O_4} \longrightarrow \underset{2\ \text{mol}}{2CO_2} + Na_2C_4O_4 + H_2O$$

⇒ In the reaction, number of mole of CO_2 produced.

$$n = \frac{pV}{RT} = \frac{1\ \text{bar} \times 0.25 \times 10^{-3}\ \text{L}}{0.082\ \text{L atm K}^{-1}\text{mol}^{-1} \times 298.15\ \text{K}}$$

$$= 1.02 \times 10^{-5}\ \text{mol}$$

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Number of mole of $NaHCO_3$

$$= \frac{\text{Weight of } NaHCO_3}{\text{Molecular mass of } NaHCO_3}$$

$\therefore\ w_{NaHCO_3} = 1.02 \times 10^{-5} \times 84 \times 10^3$ mg

$= 0.856$ mg

$\Rightarrow NaHCO_3\ \% = \frac{0.856}{10} \times 100 = 8.56\%$

31 The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing 10^{-3} M $CaSO_4$ is (Molar mass of $CaSO_4$ = 136 g mol^{-1})

[2019, 12 Jan Shift-I]

(a) 100 ppm (b) 10 ppm
(c) 50 ppm (d) 90 ppm

Ans. ***(a)***

Hardness of water sample can be calculated in terms of ppm concentration of $CaCO_3$.

Given, molarity = 10^{-3} M

i.e. 1000 mL of solution contains 10^{-3} mole of $CaCO_3$.

$\therefore$ Hardness of water = ppm of $CaCO_3$

$$= \frac{10^{-3} \times 1000}{1000} \times 10^6$$

$= 100$ ppm

32 The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is 1:4. The ratio of number of their molecule is **[JEE Main 2014]**

(a) 1:4 (b) 7:32
(c) 1:8 (d) 3:16

Ans. ***(b)***

The number of moles is given by

$$n = \frac{\text{weight}(w)}{\text{molecular weight}\ (M)}$$

Thus, ratio of moles of O_2 and N_2 is given by

$$\frac{n_{O_2}}{n_{N_2}} = \left(\frac{W_{O_2}/M_{O_2}}{W_{N_2}/M_{N_2}}\right) = \left(\frac{W_{O_2}}{W_{N_2}}\right)\left(\frac{M_{N_2}}{M_{O_2}}\right)$$

$$= \left(\frac{1}{4}\right) \times \left(\frac{28}{32}\right) = \frac{7}{32}$$

Hence, ratio of n_{O_2} and n_{N_2} is 7:32.

33 The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2M HCl will be **[JEE Main 2013]**

(a) 0.875 M (b) 1.00 M
(c) 1.75 M (d) 0.0975 M

Ans. ***(a)***

The molarity of a resulting solution is given by

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

$$= \frac{750 \times 0.5 + 250 \times 2}{750 + 250} = \frac{875}{1000}$$

$= 0.875$ M

34 The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is **[AIEEE 2012]**

(a) 0.50 M (b) 1.78 M
(c) 1.02 M (d) 2.05 M

Ans. ***(d)***

Total mass of solution = 1000 g water + 120 g urea = 1120 g

Density of solution = 1.15 g / mL

Thus, volume of solution $= \frac{\text{mass}}{\text{density}}$

$$= \frac{1120\ \text{g}}{1.15\ \text{g/mL}}$$

$= 973.91$ mL

$= 0.974$ L

Moles of solute $= \frac{120}{60} = 2$ mol

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{volume (L) of solution}}$$

$$= \frac{2\ \text{mol}}{0.974\ \text{L}} = 2.05\ \text{mol L}^{-1}$$

35 The molality of a urea solution in which 0.0100 g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm^3 of water at STP is **[AIEEE 2011]**

(a) 5.55×10^{-4} M (b) 33.3M
(c) 3.33×10^{-2} M (d) 0.555 M

Ans. ***(a)***

$$\text{Molality} = \frac{\text{moles of the solute}}{\text{mass of the solvent in kg}}$$

$$\text{Moles of urea}\ (n_{urea}) = \frac{0.0100\ \text{g}}{60\ \text{g mol}^{-1}}$$

Mass of 1000 mL of solution

= volume × density

$$= 300\ \text{mL} \times \frac{1\ \text{g}}{\text{mL}}$$

$[\because 1\ dm^3 = 1000\ \text{mL}]$

$= 300$ g

Mass of solvent = 300 g − 0.0100 g

$= 299.9$ g

$= 0.2999$ kg

$$\text{Molality} = \frac{0.0100}{60 \times 0.2999}$$

$= 5.55 \times 10^{-4}$ mol kg^{-1}

36 How many moles of magnesium phosphate, $Mg_3(PO_4)_2$ will contain 0.25 mole of oxygen atoms? **[AIEEE 2006]**

(a) 0.02 (b) 3.125×10^{-2}
(c) 1.25×10^{-2} (d) 2.5×10^{-2}

Ans. ***(b)***

8 moles of O-atom are contained by 1 mole $Mg_3(PO_4)_2$.

Hence, 0.25 moles of O-atom are contained by

$$= \frac{1}{8} \times 0.25\ \text{mol}\ Mg_3(PO_4)_2 = 3.125 \times 10^{-2}$$

37 Number of atoms in 560 g of Fe (atomic mass = 56 g mol^{-1}) is

(a) twice that of 70 g N **[AIEEE 2002]**
(b) half that of 20 g H
(c) Both (a) and (b)
(d) None of the above

Ans. ***(c)***

560 g of Fe

$$\text{Number of moles} = \frac{560\ \text{g}}{56\ \text{g mol}^{-1}} = 10\ \text{mol}$$

For 70 g of N, 14 g N = 1 mol of N-atom

70 g N = 5 mol of N-atom

For 20 g of H, 1 g H = 1 mol of H-atom

20 g H ≡ 20 mol of H-atom

TOPIC 4

Stoichiometric and Volumetric Calculations

38 Sodium oxide reacts with water to produce sodium hydroxide. 20.0 g of sodium oxide is dissolved in 500 mL of water. Neglecting the change in volume, the concentration of the resulting NaOH solution is ..... $\times 10^{-1}$ M. (Nearest integer)

[Atomic mass : Na = 23.0, O = 16.0, H = 1.0] **[2021, 31 Aug Shift-II]**

Ans. ***(13)***

For the reaction,

$$\underset{1\ \text{mol}}{Na_2O} + H_2O \longrightarrow \underset{x\ \text{mol}}{2NaOH}$$

$\frac{20}{62}$ mol

Moles of NaOH formed $\Rightarrow x = \frac{20}{62} \times 2$

Concentration of NaOH

$$= \frac{\text{Moles of NaOH}}{\text{Volume of solution (in litre)}}$$

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$$= \frac{\frac{20}{62} \times 2}{\frac{500}{1000}} = 1.29\ M = 13 \times 10^{-1}\ M$$

39 100 g of propane is completely reacted with 1000 g of oxygen. The mole fraction of carbon dioxide in the resulting mixture is $x \times 10^{-2}$. The value of x is ..... . (Nearest integer) [Atomic weight : H = 1.008, C = 12.00, O =16.00]

[2021, 27 Aug Shift-II]

Ans. ***(19)***

For the reaction,

$$CH_3CH_2CH_3(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$
$$1 : 5 \qquad 3 : 4$$

1 mole of propane reacts completely with 5 moles of oxygen to form 3 moles of carbon dioxide and 4 moles of steam.

44 g of propane = 1 mole of propane

$$100\text{ g of propane} = \frac{1}{44} \times 100 = 2.27\text{ mol}$$

32 g of O_2 = 1 mole of O_2

$$1000\text{ g of } O_2 = \frac{1}{32} \times 1000 = 31.25\text{ moles}$$

$\therefore$ 2.27 moles of propane requires $5 \times 2.27 = 11.35$ moles of O_2

moles of CO_2 formed

$= 3 \times 2.7 = 6.681$ mol of CO_2

$$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

	1	:	5		3	:	4
at $t = 0$	2.27 mol		31.25 mol		0		0
at $t = t$	0		31.25 – (5 × 2.27) 19.90 mol		3 × 2.27 6.81 mol		4 × 2.27 9.08 mol

When reaction is completed 19.90 moles of O_2, 6.81 moles of CO_2 and 9.08 moles of steam are left in the flask.

Mole fraction of

$$CO_2 = \frac{\text{Moles of } CO_2(g)}{\text{Total number of moles}} = \frac{6.81}{19.90 + 6.81 + 9.08} = 0.19$$

$$x \times 10^{-2} = 0.19 \Rightarrow x = 19$$

40 A chloro compound *A*,

(i) Forms aldehydes on ozonolysis followed by the hydrolysis.

(ii) When vaporised completely, 1.53 g of *A* gives 448 mL of vapour at STP.

The number of carbon atoms in a molecule of compound *A* is ..... .

[2021, 26 Aug Shift-II]

Ans. ***(3)***

Given, 448 mL of *A* gives 1.53 g of vapours.

$$\therefore \text{ 22400 mL of } A \text{ gives} = \frac{1.53}{445} \times 22400$$
$$= 76.50\text{ g of } A$$

$\therefore$ Molecular mass is 76.5.

$\therefore$ The possible compound is

$$CH_3—CH = CH—Cl$$

On ozonolysis followed by hydrolysis, it gives aldehyde as follows.

$$H_3CHC = CH — Cl \xrightarrow[Zn/H_2O]{O_3} CH_3 — \underset{\underset{O}{\|}}{CH} \text{ (Aldehyde)} + Cl — \underset{\underset{H}{|}}{C} = O$$

The compound (*A*) $CH_3—CH = CH—Cl$ (chloropropene) has 3 carbon atoms.

41 4g equimolar mixture of NaOH and Na_2CO_3 contains x g of NaOH and y g of Na_2CO_3. The value of x is ..... g. (Nearest integer)

[2021, 20 July Shift-II]

Ans. ***(1)***

Total mass = 4 g (given)

Mass of NaOH = x g

Mass of Na_2CO_3 = y g

$$x + y = 4$$

$$\frac{\text{Mass of NaOH}}{\text{Molar mass of NaOH}} = \frac{\text{Mass of } Na_2CO_3}{\text{Molar mass of } Na_2CO_3}$$

$$\frac{x}{40} = \frac{y}{106} \quad \text{(Equimolar)}$$

$$y = \left(\frac{106}{40}\right)x \Rightarrow x + \frac{106}{40}x = 4$$

$$x + 2.065x = 4 \Rightarrow 3.065x = 4$$

$$x = 1.096\text{ g} \Rightarrow x \simeq 1$$

42 250 mL of 0.5 M NaOH was added to 500 mL of 1 M HCl. The number of unreacted HCl molecules in the solution after complete reaction is ..... $\times 10^{21}$. (Nearest integer) ($N_A = 6.022 \times 10^{23}$)

[2021, 20 July Shift-I]

Ans. ***(226)***

We know that, number of moles

$= V_L \times$ molarity

and number of millimoles

$= V_{mL} \times$ molarity

So, millimoles of

NaOH = $250 \times 0.5 = 125$

Millimoles of HCl = $500 \times 1 = 500$

Now, reaction is

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

At $t = 0$,	125	500	0	0
At $t = t$,	0	375	125	125

125 millimoles of NaOH reacts with 125 millimoles of HCl.

So, millimoles of HCl left = 375

Moles of HCl = 375×10^{-3}

Number of HCl molecules

= Avogadro's constant (N_A) × moles of HCl

$= 6.022 \times 10^{23} \times 375 \times 10^{-3}$

$= 225.8 \times 10^{21} = 226 \times 10^{21}$

Therefore, answer is 226.

43 10.0 mL of Na_2CO_3 solution is titrated against 0.2 M HCl solution. The following titre values were obtained in 5 readings. 4.8 mL, 4.9 mL, 5.0 mL, 5.0 mL and 5.0 mL based on these readings and convention of titrimetric estimation of concentration of Na_2CO_3 solution is ..... mM (Round off to the nearest integer).

[2021, 18 March Shift-II]

Ans. ***(50)***

10.0 mL of Na_2CO_3 solution is titrated against 0.2 M HCl.

Volume of Na_2CO_3 solution (mL)	Volume of 0.2 M HCl solution (mL)	Mean volume of HCl (mL)
10	4.8	5.0
10	4.9	
10	5.0	
10	5.0	
10	5.0	

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

10 mL Na_2CO_3 ; $M_{Na_2CO_3} = ?$; 5 mL $0.2\ M_{HCl}$

M_{eq} of Na_2CO_3 = M_{eq} of HCl

$$M_{Na_2CO_3} \times 10 \times 2 = 0.2 \times 5 \times 1$$

$$M_{Na_2CO_3} = 5 \times 10^{-2}\ M = 50 \times 10^{-3}\ M$$

$= 50$ mM

44 Complete combustion of 750 g of an organic compound provides 420 of CO_2 and 210 g of H_2O. The percentage composition of carbon and hydrogen in organic compound is 15.3 and ..... respectively (Round off to the nearest integer).

[2021, 16 March Shift-I]

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Ans. ***(3)***

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow x\,CO_2 + \frac{y}{2}H_2O$$

Any hydrocarbon, on combustion gives CO_2 and H_2O. This is Liebig's method for estimation of 'C' and 'H' percentage.

Mass of water formed = 210 g

18 g of H_2O contains = 2 g of hydrogen

210 g of H_2O contains $= \left(\frac{2}{18} \times 210 = \frac{70}{3}\right)$ g

of hydrogen.

Given, mass of organic compound = 750 g

Percentage of hydrogen

$$= \frac{\text{Mass of hydrogen}}{\text{Mass of organic compound}} \times 100$$

$$= \frac{70}{3 \times 750} \times 100 = 3.11\%$$

Nearest integer = 3

45 Complete combustion of 1.80 g of an oxygen containing compound ($C_xH_yO_z$) gave 2.64 g of CO_2 and 1.08 g of H_2O. The percentage of oxygen in the organic compound is

[2021, 25 Feb Shift-I]

(a) 50.33 (b) 53.33
(c) 63.53 (d) 51.63

Ans. ***(b)***

$$\underset{1.8\text{ g}}{C_xH_yO_z} + O_2 \longrightarrow \underset{2.64\text{ g}}{CO_2} + \underset{1.08\text{ g}}{H_2O}$$

$$n_C = \underset{\text{(Moles)}}{n_{CO_2}} = \frac{2.64\,(\text{Given mass})}{44\,(\text{Molecular mass})} = 0.06$$

$$n_H = 2 \times n_{H_2O} = \frac{1.08}{18} \times 2 = 0.12$$

Weight of oxygen in $C_xH_yO_z$

$$= 1.80 - 12 \times \frac{2.64}{44} - \frac{1.08}{18} \times 2$$

$$= 1.80 - 0.72 - 0.12 = 0.96\text{ g}$$

% of oxygen by weight

$$= \frac{0.96}{1.80} \times 100 = 53.33\%$$

46 The formula of a gaseous hydrocarbon, which requires 6 times of its own volume of O_2 for complete oxidation and produces 4 times its own volume of CO_2 is C_xH_y. The value of y is ..... .

[2021, 24 Feb Shift II]

Ans. ***(8)***

Combustion reaction :

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \longrightarrow xCO_2(g) + \frac{y}{z}H_2O(l)$$

Suppose, volume of C_xH_y is V and volume of O_2 is 6 times greater than $C_xH_y = 6V$

then volume of $xCO_2 \Rightarrow Vx = 4V$

$$x = 4$$

Since, $V_{O_2} = 6 \times V_{C_xH_y}$

$$V\left(x + \frac{y}{4}\right) = 6V$$

$$\left(x + \frac{y}{4}\right) = 6 \quad \ldots(i)$$

Put value of $x = 4$ in Eq. (i)

We get, $4 + \frac{y}{4} = 6 \Rightarrow y = 8$

47 1.86 g of aniline completely reacts to form acetanilide. 10% of the product is lost during purification. Amount of acetanilide obtained after purification (in g) is ..... $\times 10^{-2}$.

[2021, 24 Feb Shift-II]

Ans. ***(432)***

Reaction

$$\underset{\substack{\text{Aniline}\\\text{Mol. wt} = 98}}{C_6H_5NH_2} \xrightarrow[\text{Efficiency}]{90\%} \underset{\substack{\text{Acetanilide}\\\text{(mol. wt. = 135)}}}{C_6H_5-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3}$$

Given, weight = 1.86 g

Here, 1 mole of aniline gives 1 mole of acetanilide

$\therefore$ mole of aniline = mole of acetanilide

$$\Rightarrow \quad \frac{1.86}{93} = \frac{W_{\text{Acetanilide}}}{135}$$

$$W_{\text{Acetanilide}} = \frac{1.86 \times 135}{93}\text{ g} = 2.70\text{ g}$$

But efficiency of reaction is 90% only.

Hence, mass of acetanilide produced

$$= 2.70 \times \frac{90}{100}\text{ g} = 2.43\text{ g} = 243 \times 10^2\text{ g}$$

$$x = 243$$

48 The ratio of the mass percentages of 'C' and H' and 'C and O' of a saturated acyclic organic compound 'X' are 4 : 1 and 3 : 4 respectively. Then, the moles of oxygen gas required for complete combustion of two moles of organic compound 'X' is ..... .

[2020, 2 Sep Shift-II]

Ans. ***(5)***

For the molecular formula, $C_nH_{2n+2}O_2$

(M=Molar mass)

$$C\% = \frac{12n}{M} \times 100,\ H\% = \frac{2n+2}{M} \times 100,$$

$$O\% = \frac{32}{M} \times 100$$

To be saturated and alicyclic, $n = 2$, is,

$$C\% = \frac{24}{M} \times 100,\ H\% = \frac{6}{M} \times 100 \text{ and}$$

$$O\% = \frac{32}{M} \times 100$$

$$\Rightarrow \quad C\% : H\% = 24 : 6 = 4 : 1$$

$$C\% : O\% = 24 : 32 = 3 : 4$$

So, X is $C_2H_6O_2$ and its combination equation is

$$C_2H_6O_2 + \left(2 + \frac{6}{4} - \frac{1}{2}\right)O_2 \longrightarrow 2CO_2 + \frac{6}{2}H_2O$$

$$\Rightarrow \underset{1\text{ mol}}{C_2H_6O_2} + \frac{5}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$\frac{5}{2}\text{ mol}$$

$$2\text{ mol} \times \frac{5}{2} \times 2 = 5\text{ mol of } O_2 \text{ will be required.}$$

49 The volume (in mL) of 0.1 N NaOH required to neutralise 10 mL of 0.1 N phosphonic acid is ..... .

[2020, 3 Sep Shift-II]

Ans. ***(10)***

$$\text{Base} + \text{Acid} \longrightarrow \text{Salt} + H_2O$$

$$\underset{\text{Base}}{NaOH} + \underset{\text{Phosphonic acid}}{H_3PO_3} \longrightarrow \underset{\text{Salt}}{NaH_2PO_3} + \underset{\text{Water}}{H_2O}$$

$$\text{Given} \begin{cases} 0.1\text{ N} & 0.1\text{ N} \\ V = ? & 10\text{ mL} \end{cases}$$

On dilution $(N_1V_1)_{NaOH} = (N_2V_2)_{H_2PO_3}$

$$0.1V_1 = 0.1 \times 10\text{ mL} \Rightarrow V_1 = \frac{0.1 \times 10\text{ mL}}{0.1}$$

$$V_1 = 10\text{ mL}$$

Volume of NaOH = 10 mL

50 The mass of ammonia in grams produced when 2.8 kg of dinitrogen quantitatively reacts with 1 kg of dihydrogen is ..... .

[2020, 4 Sep Shift-I]

Ans. ***(3400)***

$$\underset{1\text{ mol}}{N_2} + \underset{3\text{ mol}}{3H_2} \longrightarrow \underset{2\text{ mol}}{2NH_3}$$

Molecular weight of N_2(kg) = 0.028 kg/mol

Mass of 'N' atom = 14 g

Then, mass of N_2 molecule = 28 g = 0.028 kg/mol

Molecular weight of H_2 = 2 g

Here, $3H_2$ is $= 3 \times 2 = 6\text{ g} = 0.006$ kg/mol

Molecular weight of NH_3 is = 17 g

Molecular weight of $2NH_3$(kg) = 0.034 kg/mol

0.028 kg N_2 require hydrogen = 0.006 kg

$$1\text{ kg } N_2 \text{ require} = \frac{0.006}{0.028}$$

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2.8 kg N_2 (limiting reagent) require

$$= \frac{0.006}{0.028} \times 2.8 = 0.6 \text{ kg } H_2 \text{(Excess)}$$

Then 0.6 kg H_2 is present in excess and N_2 will be limiting reagent.

$$0.028 \text{ kg } N_2 \xrightarrow{\text{Excess}} 0.034 \text{ kg of } NH_3$$

$$1 \text{ kg } N_2 \longrightarrow \frac{0.034}{0.028}$$

$$2.8 \text{ kg } N_2 \longrightarrow \frac{0.034}{0.028} \times 2.8$$

$$= 3.4 \text{ kg or } 3400 \text{ g}$$

Amount of $NH_3 = 3400$ g

51 The minimum number of moles of O_2 required for complete combustion of 1 mole of propane and 2 moles of butane is ..... .

[2020, 5 Sep Shift-I]

Ans. ***(18)***

Combustion of propane

$$\underset{\text{Propane}}{C_3H_8(g)} + 5\,O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

For 1 mole propane combustion 5 mole O_2 is required.

Combustion of butane

$$\underset{\substack{\text{Butane}\\ 2 \text{ mol}}}{C_4H_{10}(g)} + \frac{13}{2}\,O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$$

For 2 moles of butane 13 moles of O_2 is required.

Hence, minimum number of moles of O_2 required to oxidise 1 mole of propane and 2 moles of butane $= 5 + 2 \times \frac{13}{2} = 18$

52 The volume, in mL, of 0.02 M $K_2Cr_2O_7$ solution required to react with 0.288 g of ferrous oxalate in acidic medium is ..... .

(Molar mass of Fe = 56 g mol^{-1})

[2020, 5 Sep Shift-II]

Ans. ***(50)***

m eq. of $K_2Cr_2O_7 = m$ eq. FeC_2O_4

$$K_2Cr_2O_7 + 7H_2SO_4 + FeCrO_4 \rightarrow Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 4CO_2 + 7H_2O$$

$$FeC_2O_4 + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + CO_2 + Cr^{3+}$$

$$V \times 0.02 \times 6 = \frac{0.288 \times 3 \times 1000}{144}$$

$\Rightarrow V = 50$ mL

53 The ammonia (NH_3) released on quantitative reaction of 0.6 g urea (NH_2CONH_2) with sodium hydroxide (NAOH) can be neutralised by **[2020, 7 Jan Shift-II]**

(a) 100 mL of 0.2 N HCl
(b) 200 mL of 0.4 N HCl
(c) 200 mL of 0.2 N HCl
(d) 100 mL of 0.1 N HCl

Ans. ***(a)***

$$\underset{(M=60)}{NH_2CONH_2} + 2\,NaOH \longrightarrow 2\,NH_3 + Na_2CO_3$$

No. of moles of urea

= Given mass/molar mass

$$= \frac{0.6}{60} = 0.01 \text{ mol } NH_2CONH_2$$

$\therefore$ It gives 0.02 mol NH_3 as per the equation.

To neutralise it, 0.02 equivalents of HCl needed.

As we know, no. of equivalents of HCl = Normality × Volume

Therefore,

(a) $100 \times 10^{-3} \times 0.2 = 0.02$.
(b) $200 \times 10^{-3} \times 0.4 = 0.08$
(c) $200 \times 10^{-3} \times 0.2 = 0.04$
(d) $100 \times 10^{-3} \times 0.1 = 0.01$

Thus, option (a) is correct.

54 The volume (in mL) of 0.125 M $AgNO_3$ required to quantitatively precipitate chloride ions in 0.3 g of $[Co(NH_3)_6]Cl_3$ is ..... .

$M_{[Co(NH_3)_6]Cl_3} = 267.46$ g/mol

$M_{AgNO_3} = 169.87$ g/mol

[2020, 8 Jan Shift-I]

Ans. ***(26.92)***

Given, Mass of $[Co(NH_3)_6]Cl_3 = 0.3$ g

Molar mass = 267.46 g mol^{-1}

$$\therefore \quad n = \frac{0.3}{267.46} \text{ mol}$$

From the formula, 1 mol complex will give 3 mol Cl^-.

$$\therefore \quad n_{Cl^-} = \frac{0.3}{267.46} \times 3 = \frac{0.9}{267.46}$$

The precipitation reaction is takes place as follows :

$$\underset{(0.3g)}{[Co(NH_3)_6]Cl_3} + \underset{(V\text{mL},0.125g)}{3AgNO_3} \longrightarrow 2AgCl$$

$$\therefore \quad \frac{0.3 \times 3}{267.46} = 0.125 \times V \times 10^{-3}$$

$\therefore$ Volume of $AgNO_3$ (in mL)

$$= \frac{0.9 \times 1000}{0.125 \times 267.46}$$

$$= 26.92 \text{ mL}.$$

This value may vary from 26.60 to 27.00.

55 $NaClO_3$ is used, even in spacecrafts, to produce O_2. The daily consumption of pure O_2 by a person is 492 L at 1 atm 300 K. How much amount of $NaClO_3$, in grams, is required to produce O_2 for the daily consumption of a person at 1 atm, 300 K ..... ?

$$NaClO_3(s) + Fe(s) \rightarrow O_2(g) + NaCl(s) + FeO(s)$$

$R = 0.082 \text{ L atm mol}^{-1}\text{K}^{-1}$

[2020, 8 Jan Shift-II]

Ans. ***(2130)***

Volume of $O_2 = 492$ L

$$\therefore \quad n = \frac{pV}{RT}$$

$$= \frac{1 \text{ atm} \times 492 \text{ L}}{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

$$= \frac{492}{8.2 \times 3} \text{ mol}$$

From the reaction,

$$NaClO_3(s) + Fe(s) \longrightarrow O_2(g) + NaCl(s) + FeO(s)$$

$$n_{NaClO_3} = n_{O_2} = \frac{492}{8.2 \times 3} = 20 \text{ mol}$$

$m_{NaClO_3} = n \times$ molar mass of $NaClO_3 (= 106.5)$

$$= 20 \times 106.5 = 2130 \text{ g}$$

The value in different situations may range from 2120 to 2140.

56 The strength of 11.2 volume solution of H_2O_2 is [Given that molar mass of H = 1 g mol^{-1} and O = 16 g mol^{-1}]

[2019, 8 April Shift-II]

(a) 1.7% (b) 34%
(c) 13.6% (d) 3.4%

Ans. ***(d)***

11.2 volume of H_2O_2 means that 1 mL of this H_2O_2 will give 11.2 mL of oxygen at STP.

$$\underset{2 \times 34 \text{ g}}{2H_2O_2(l)} \longrightarrow \underset{22.4 \text{ L at STP}}{O_2(g)} + 2H_2O(l)$$

22.4 L of O_2 at STP is produced from $H_2O_2 = 68$ g

$\therefore$ 11.2 L of O_2 at STP is produced from

$$H_2O_2 = \frac{68}{22.4} \times 11.2$$

$$= 34 \text{ g}$$

$\therefore$ 34 g of H_2O_2 is present in 1000 g of solution

$$\therefore \quad \%\ w/w = \frac{34}{1000} \times 100 = 3.4\%.$$

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57 For a reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, identify dihydrogen ($H_2$) as a limiting reagent in the following reaction mixtures. **[2019, 9 April Shift-I]**

(a) 56 g of N_2 + 10 g of H_2
(b) 35 g of N_2 + 8 g of H_2
(c) 14 g of N_2 + 4 g of H_2
(d) 28 g of N_2 + 6 g of H_2

Ans. ***(a)***

Key Idea The reactant which is present in the lesser amount, i.e. which limits the amount of product formed is called limiting reagent.

When 56 g of N_2 + 10 g of H_2 is taken as a combination then dihydrogen (H_2) act as a limiting reagent in the reaction.

$$\underset{2\times14\,g\ =\ 28\,g}{N_2(g)} + \underset{3\times2\,g\ =\ 6\,g}{3H_2(g)} \longrightarrow \underset{2(14+3)\ =\ 34\,g}{2NH_3(g)} \quad ...(i)$$

28 g N_2 requires 6 g H_2 gas.

56 g of N_2 requires $\frac{6\,g}{28\,g}\times 56\,g = 12\,g$ of H_2

12 g of H_2 gas is required for 56 g of N_2 gas but

only 10 g of H_2 gas is present in option (a).

Hence, H_2 gas is the limiting reagent.

In option (b), i.e. 35 g of N_2 + 8 g of H_2.

As 28 g N_2 requires 6 g of H_2.

35 g N_2 requires $\frac{6\,g}{28\,g}\times 35\,g\ H_2$

$\Rightarrow$ 7.5 g of H_2

Here, H_2 gas does not act as limiting reagent since 7.5 g of H_2 gas is required for 35 g of N_2 and 8 g of H_2 is present in reaction mixture. Mass of H_2 left unreacted = 8 – 7.5 g of H_2. = 0.5 g of H_2.

Similarly, in option (c) and (d), H_2 does not act as limiting reagent.

For 14g of N_2 + 4 g of H_2.

As we know 28g of N_2 reacts with 6 g of H_2.

14 g of N_2 reacts with $\frac{6}{28}\times 14\,g$ of H_2

3 g of H_2

For 28 g of N_2 + 6 g of H_2, i.e. 28 g of N_2 reacts with 6 g of H_2 [by equation (i)].

58 At 300 K and 1 atmospheric pressure, 10 mL of a hydrocarbon required 55 mL of O_2 for complete combustion and 40 mL of CO_2 is formed. The formula of the hydrocarbon is **[2019, 10 April Shift-I]**

(a) C_4H_7Cl (b) C_4H_6
(c) C_4H_{10} (d) C_4H_8

Ans. ***(b)***

In eudiometry,

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \xrightarrow[1\,atm]{300\,K} x\,CO_2 + \frac{y}{2}H_2O$$

1 mol	$\left(x+\frac{y}{4}\right)$ mol	x mol
1 mL	$\left(x+\frac{y}{4}\right)$ mL	x mL
10 mL	$\left(x+\frac{y}{4}\right)\times 10$ mL	10x mL

Given, (i) $V_{CO_2} = 10x = 40\ mL \Rightarrow x = 4$

(ii) $V_{O_2} = 10\left(x+\frac{y}{4}\right)mL = 55\ mL$

$\Rightarrow \quad 10\left(4+\frac{y}{4}\right) = 55 \qquad [\because x = 4]$

$\Rightarrow \quad 40 + \frac{y\times 10}{4} = 55$

$\Rightarrow \quad y\times\frac{10}{4} = 15 \Rightarrow y = 15\times\frac{4}{10} = 6$

So, the hydrocarbon (C_xH_y) is C_4H_6.

59 The minimum amount of $O_2(g)$ consumed per gram of reactant is for the reaction (Given atomic mass : Fe = 56, O = 16, Mg = 24, P = 31, C = 12, H = 1) **[2019, 10 April Shift-II]**

(a) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

(b) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$

(c) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

(d) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

Ans. ***(b)***

(a) $\underset{44g}{C_3H_8(g)} + \underset{160g}{5O_2(g)} \longrightarrow 3CO_2(g) + 4H_2O(l)$

$\Rightarrow$ 1g of reactant $= \frac{160}{44}$ g of O_2 consumed = 3.64 g

(b) $\underset{124g}{P_4(s)} + \underset{160g}{5O_2(g)} \longrightarrow P_4O_{10}(s)$

$\Rightarrow$ 1g of reactant $\frac{160}{124}$ g of O_2 consumed = 1.29 g

(c) $\underset{244g}{4Fe(s)} + \underset{96g}{3O_2(g)} \longrightarrow 2Fe_2O_3(s)$

$\Rightarrow$ 1 g of reactant $\frac{96}{224}$ g of O_2 consumed = 0.43 g

(d) $\underset{48\,g}{2Mg(s)} + \underset{32\,g}{O_2(g)} \longrightarrow 2MgO(s)$

$\Rightarrow$ 1 g of reactant $\frac{32}{48}$ g of O_2 consumed = 0.67 g

So, minimum amount of O_2 is consumed per gram of reactant (Fe) in reaction (c).

60 25 g of an unknown hydrocarbon upon burning produces 88 g of CO_2 and 9 g of H_2O. This unknown hydrocarbon contains **[2019, 12 April Shift-II]**

(a) 20 g of carbon and 5 g of hydrogen
(b) 22 g of carbon and 3 g of hydrogen
(c) 24 g of carbon and 1 g of hydrogen
(d) 18 g of carbon and 7 g of hydrogen

Ans. ***(c)***

Hydrocarbon containing C and H upon burning produces CO_2 and water vapour respectively. The equation is represented as

$$C_xH_y + (x + y/4)O_2 \longrightarrow xCO_2 + (y/2)H_2O$$

Mass of carbon $= \frac{12}{44}\times$ mass of CO_2

$= \frac{12}{44}\times 88\,g = 24\,g$

Mass of hydrogen $= \frac{2}{18}\times$ mass of H_2O

$= \frac{2}{18}\times 9 = 1\,g$

So, the unknown hydrocarbon contains 24 g of carbon and 1g of hydrogen.

61 For the following reaction, the mass of water produced from 445 g of $C_{57}H_{110}O_6$ is :

$$2C_{57}H_{110}O_6(s) + 163O_2(g) \longrightarrow 114CO_2(g) + 110H_2O(l)$$

[2019, 10 Jan Shift-II]

(a) 490 g (b) 495 g (c) 445 g (d) 890 g

Ans. ***(b)***

$$2\,C_{57}H_{110}O_6(s) + 163\,O_2(g) \longrightarrow 110\,H_2O(l) + 114\,CO_2(g)$$

Molecular mass of $C_{57}H_{110}O_6$

$= 2\times(12\times 57 + 1\times 110 + 16\times 6)\,g$

$= 1780\,g$

Molecular mass of $110\,H_2O$

$= 110\,(2 + 16) = 1980\,g$

1780 g of $C_{57}H_{110}O_6$ produced = 1980 g of H_2O.

445g of $C_{57}H_{110}O_6$ produced $= \frac{1980}{1780}\times 445$ g of H_2O = 495 of H_2O

62 A mixture of 100 mmol of $Ca(OH)_2$ and 2 g of sodium sulphate was dissolved in water and the volume was made upto 100 mL.

The mass of calcium sulphate formed and the concentration of OH^- in resulting solution, respectively, are :

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(Molar mass of $Ca(OH)_2$, Na_2SO_4 and $CaSO_4$ are74, 143 and 136 g mol^{-1}, respectively; K_{sp} of $Ca(OH)_2$ is 5.5×10^{-6})

[2019, 10 Jan Shift-I]

(a) 13.6 g, 0.28 mol L^{-1}
(b) 1.9 g, 0.28 mol L^{-1}
(c) 13.6 g, 0.14 mol L^{-1}
(d) 1.9 g, 0.14 mol L^{-1}

Ans. ***(b)***

The reaction involved is as follows :

$$Ca(OH)_2 + Na_2SO_4 \longrightarrow$$

Millimoles 100 $\frac{2\times1000}{142}=14$

at $t=0$ Milimoles 86 0

at $t=t$ [Limiting reagent]

$$CaSO_4 + 2OH^- + 2Na^+$$

0 0 0

14 28

$$\text{No. of moles} = \frac{\text{Weight}}{\text{Molecular mass}}$$

$$\therefore \text{Mass of } CaSO_4 = \frac{14}{1000}\times136 = 1.9\,g$$

Also,

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution (in L)}}$$

$\therefore$ Molarity of OH^-,

$$[OH^-] = \frac{28}{1000}\times\frac{1000}{100}$$

$$= 0.28\,mol\,L^{-1} = 0.28\,M$$

63 1 g of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2. The molar mass of M_2CO_3 in g mol^{-1} is

[JEE Main 2017]

(a) 1186 (b) 84.3 (c) 118.6 (d) 11.86

Ans. ***(b)***

$$\underset{1\,g}{M_2CO_3} + 2HCl \rightarrow 2M\,Cl + H_2O + \underset{0.01186\,mole}{CO_2}$$

Number of moles of M_2CO_3 reacted = Number of moles of CO_2 evolved

$$\frac{1}{M} = 0.01186 \quad [M = \text{molar mass of } M_2CO_3]$$

$$M = \frac{1}{0.01186} = 84.3\,g\,mol^{-1}$$

64 The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (mol. wt. = 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin?

[JEE Main 2015]

(a) $\frac{1}{103}$ (b) $\frac{1}{206}$ (c) $\frac{2}{309}$ (d) $\frac{1}{412}$

Ans. ***(d)***

We know the molecular weight of $C_8H_7SO_3Na$

$$= 12\times8 + 1\times7 + 32 + 16\times3 + 23 = 206$$

We have to find, mole per gram of resin.

$\therefore$ 1 g of $C_8H_7SO_3Na$ has number of mole

$$= \frac{\text{Weight of given resin}}{\text{Molecular weight of resin}} = \frac{1}{206}\,mol$$

Now, reaction looks like

$$2C_8H_7SO_3Na + Ca^{2+} \longrightarrow (C_8H_7SO_3)_2\,Ca + 2Na^+$$

$\because$ 2 moles of $C_8H_7SO_3Na$ combines with 1 mol Ca^{2+}

$\therefore$ 1 mole of $C_8H_7SO_3Na$ will combine with $\frac{1}{2}$ mol Ca^{2+}

$\therefore \frac{1}{206}$ mole of $C_8H_7SO_3Na$ will combine with

$$\frac{1}{2}\times\frac{1}{206}\,mol\,Ca^{2+} = \frac{1}{412}\,mol\,Ca^{2+}$$

65 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is

[JEE Main 2015]

(a) 18 mg (b) 36 mg
(c) 42 mg (d) 54 mg

Ans. ***(a)***

Given, initial strength of acetic acid = 0.06N

Final strength = 0.042 N

Volume given = 50 mL

$\therefore$ Initial m moles of CH_3COOH $= 0.06\times50 = 3$

Final m moles of CH_3COOH $= 0.042\times50 = 2.1$

$\therefore$ m moles of CH_3COOH adsorbed $= 3 - 2.1 = 0.9$ m mol

Hence, mass of CH_3COOH absorbed per gram of charcoal

$$= \frac{0.9\times60}{3}$$

($\because$ molar mass of $CH_3COOH = 60\,g\,mol^{-1}$)

$$= \frac{54}{3} = 18\,mg.$$

66 Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl because HCl **[AIEEE 2008]**

(a) gets oxidised by oxalic acid to chlorine
(b) furnishes H^+ ions in addition to those from oxalic acid
(c) reduces permanganate to Mn^{2+}
(d) oxidises oxalic acid to carbon dioxide and water

Ans. ***(c)***

Titration of oxalic acid by $KMnO_4$ in the presence of HCl gives unsatisfactory result because HCl is a better reducing agent than oxalic acid and HCl reduces preferably MnO_4^- to Mn^{2+}.

67 In the reaction,

$$2Al(s) + 6HCl(aq) \longrightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$$

[AIEEE 2007]

(a) 6L HCl (aq) is consumed for every 3L H_2 (g) produced
(b) 33.6 L H_2 (g) is produced regardless of temperature and pressure for every mole Al that reacts
(c) 67.2 L H_2 (g) at STP is produced for every mole Al that reacts
(d) 11.2 L H_2 (g) at STP is produced for every mole HCl (aq) consumed

Ans. ***(d)***

$$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$$

From the equation, it is clear that,
6 mol of HCl produces 3 mol of H_2

or 1 mole of HCl $= \frac{3\times22.4}{6}$ L of H_2

$= 11.2$ L of H_2

68 What volume of hydrogen gas, at 273 K and 1 atm pressure will be consumed in obtaining 21.6 g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen? **[AIEEE 2003]**

(a) 89.6 L (b) 67.2 L
(c) 44.8 L (d) 22.4 L

Ans. ***(b)***

$$2BCl_3 + 3H_2 \longrightarrow 2B + 6HCl$$

2 mol 3 mol 2 mol

21.6 g

21.6 g B = 2 mol B $\equiv$ 3 mol H_2

$pV = nRT$

$$\Rightarrow V = \frac{nRT}{p}$$

$$= \frac{3\times0.0821\times273}{1} = 67.2\,L$$

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02

States of Matter

TOPIC 1
Gaseous State

01 An empty LPG cylinder weight 14.8 kg. When full, it weight 29.0 kg and shows a pressure of 3.47 atm. In the course of use at ambient temperature, the mass of the cylinder is reduced to 23.0 kg. The final pressure inside of the cylinder is ..... atm. (Nearest integer)

(Assume LPG of be an ideal gas)

[2021, 1 Sep Shift-II]

Ans. ***(2)***

Weight of empty LPG cylinder = 14.8 kg

Weight of full LPG cylinder = 29 kg

$\therefore$ Weight of gas = 29 – 14.8 = 14.2 kg

If weight of full LPG cylinder = 23 kg

then weight of gas used = 29 – 23 = 6 kg at ambient temperature.

From ideal gas equaiton, $pV = nRT$

or $pV = \dfrac{\text{Weight of solute}}{\text{Molecular mass of solute}} \times RT$

or $pV = \dfrac{W}{M} \times RT$

Applying ideal gas to LPG cylinder when gas is full,

$$pV = nRT$$

$$3.47 \text{ atm} \times V = \frac{14.2 \text{ kg}}{M} \times RT \quad \text{...(i)}$$

Applying ideal gas to LPG cylinder when gas is reduced to 23 kg at ambient temperature,

$$pV = nRT$$

$$p \times V = \frac{8.\ 2 \text{ kg}}{M} \times RT \quad \text{...(ii)}$$

Divide Eq. (i) by (ii)

$$\frac{3.47 \times V}{p \times V} = \frac{\dfrac{14.2 \text{ kg } RT}{M}}{\dfrac{8.2 \text{ kg} \times RT}{M}}$$

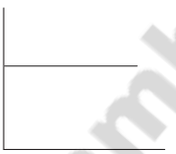
$$\frac{3.47}{p} = \frac{14.2}{8.2}$$

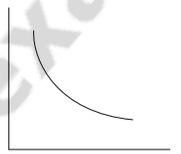
$$\Rightarrow \quad p = \frac{3.47 \times 41}{71} = 2.003 \text{ atm}$$

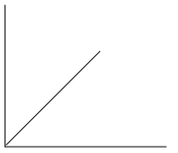
Hence, answer is 2.

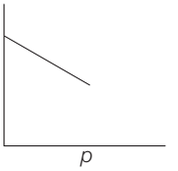
02 Which one of the following is the correct pV *vs* p plot at constant temperature for an ideal gas ? (p and V stand for pressure and volume of the gas respectively)

[2021, 31 Aug Shift-I]

(a) 

(b) 

(c) 

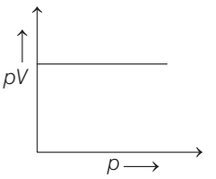
(d) 

Ans. ***(a)***

From ideal gas equation, $pV = nRT$

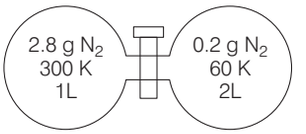
Given that, pV = constant, since temperature is constant.

Hence, graph for pV *vs* p will be



Hence, correct option is (a).

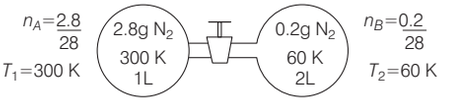
03 Two flasks I and II shown below are connected by a valve of negligible volume. **[2021, 27 Aug Shift-II]**

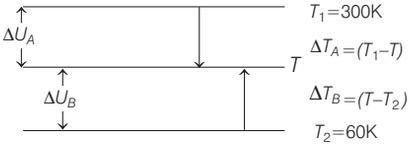


When the valve is opened, the final pressure of the system in bar is $x \times 10^{-2}$. The value of x is ..... . (Integer answer)

[Assume, Ideal gas, 1 bar = 10^5 Pa, molar mass of N_2 = 28.0 g mol^{-1}; R = 8.31 J mol^{-1} K^{-1}]

Ans. ***(84)***





On mixing the temperature of gas becomes T. Internal energy lost by gas A is the internal energy gained by gas B.

$$\Delta U_A = \Delta U_B$$

$\dfrac{f}{2} n_A R \, \Delta T_A = \dfrac{f}{2} n_B R \Delta T_B$ (As both gases are diatomic, f is same on both sides)

$$n_A \Delta T_A = n_B \Delta T_B$$

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$$\frac{2.8}{28}\times(T_1-T)=\frac{0.2}{28}(T-T_2)$$

$$\frac{1}{10}(300-T)=\frac{1}{140}(T-60)$$

$$T=284\,K$$

On mixing the temperature becomes 284 K and volume becomes 3L and total number of moles becomes $(n_A+n_B)=0.10$ moles.

According to gas equation,

$$pV=(n_A+n_B)RT$$

$$=\frac{0.10\times8.3\times284}{3}$$

$$=84.18\text{ atm or }84.18\text{ bar}$$

This is final pressure of gas.

04 The unit of the van der Waals' gas equation parameter '*a*' in $\left(p+\frac{an^2}{V^2}\right)(V-nb)=nRT$ is

[2021, 27 Aug Shift-I]

(a) $kg\,ms^{-2}$ (b) $dm^3\,mol^{-1}$

(c) $kg\,ms^{-1}$ (d) $atm\,dm^6mol^{-2}$

Ans. ***(d)***

van der Waals' gas equation,

$$\left(p+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

For dimensionally correct equation, $\frac{an^2}{V}$ should have the same dimension of pressure i.e. atm.

Unit of parameter '*a*' is as follows

$$=\text{atm}\,\frac{L^2}{mol^2}=\text{atm}\,L^2\,mol^{-2}$$

$$=\text{atm}\,dm^6\,mol^{-2}.$$

05 An LPG cylinder contains gas at a pressure of 300 kPa at 27°C. The cylinder can withstand the pressure of 12×10^6 Pa. The room in which the cylinder is kept catches fire. The minimum temperature at which the bursting of cylinder will take place is ..... °C. (Nearest integer) **[2021, 25 July Shift-II]**

Ans. ***(927)***

LPG cylinder contains gas at pressure,

$$p_1=300\text{ kPa}=300\times10^3\text{ Pa}$$

$$T_1=27^\circ\text{C}$$

$$=27+273\,K=300\,K$$

Cylinder can withstand the pressure, $p_2=1.2\times10^6$ Pa

Minimum temperature (T_2) required for bursting of cylinder is ;

Formula; $\frac{p_1}{T_1}=\frac{p_2}{T_2}$

$$\frac{300\times10^3}{300}=\frac{1.2\times10^6}{T_2}$$

$$10^3=\frac{1.2\times10^6}{T_2}$$

$$\Rightarrow\quad T_2=1.2\times10^3$$

$$=1200\,K=927^\circ C$$

06 A home owner uses $4.00\times10^3\,m^3$ of methane (CH_4) gas, (assume CH_4 is an ideal gas) in a Year to heat his home. Under the pressure of 1.0 atm and 300 K, mass of gas used is $x\times10^5$ g. The value of *x* is ..... . (Nearest integer)

(Given, $R=0.083\,L\,atm\,K^{-1}mol^{-1}$)

[2021, 25 July Shift-I]

Ans. ***(26)***

Given, volume of CH_4 gas $V=4\times10^3m^3$

Temperature = 300 K

Pressure = 1 atm

Using ideal gas equation, $pV=nRT$

No. of moles of $CH_4\,(n)=\frac{pV}{RT}$

$$=\frac{4\times10^3\times1000}{0.083\times300}$$

Now, weight of $CH_4=\frac{40\times16\times10^5}{0.083\times300}$ g

$$=25.7\times10^5\text{ g}$$

$$=26\times10^5\text{ g}$$

So, value of *x* is 26.

07 The pressure exerted by a non-reactive gaseous mixture of 6.4 g of methane and 8.8 g of carbon dioxide in a 10L vessel at 27°C is ..... kPa (Round off to the nearest integer)

(Assume gases are ideal, $R=8.314\,J\,mol^{-1}\,K^{-1}$ Atomic mass, C : 12.0 u, H : 1.0 u, O : 16.0 u)

[2021, 17 March Shift-I]

Ans. ***(150)***

Given, mass of methane = 6.4 g

mass of CO_2 = 8.8 g

volume of container = 10 L

temperature = 27° C

To find, p_{total} = Total pressure

Moles of $CH_4=\frac{\text{Given mass}}{\text{Molar mass}}$

$$=\frac{6.4}{16}=0.4\,mol$$

Moles of $CO_2=\frac{8.8}{44}=0.2\,mol$

$$n_{total}=0.4+0.2=0.6\,mol$$

$$p_{total}=\frac{n_{total}RT}{V}$$

$$=\frac{0.6\times8.314\times300}{10}$$

$$=149.652=150\text{ kPa}$$

08 A certain gas obeys $p(V_m-b)=RT$. The value of $\left(\frac{\partial Z}{\partial p}\right)_T$ is $\frac{xb}{RT}$. The value of *x* is ..... . (*Z* = compressibility factor)

[2021, 26 Feb Shift-I]

Ans. ***(1)***

For 1 mole of a real gas, the van der Waals' equation is,

$$\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

At very high pressure, the equation becomes,

$$p(V_m-b)=RT$$

$$\Rightarrow\quad pV_m=RT+pb$$

$$\Rightarrow\quad \frac{pV_m}{RT}=1+\frac{pb}{RT}$$

$$\Rightarrow\quad Z=1+\frac{pb}{RT}$$

$$[\because Z=\frac{pV_m}{RT}=\text{compressibility}]$$

$$\therefore\quad \left(\frac{\delta Z}{\delta p}\right)_T=0+\frac{b}{RT}=\frac{b}{RT}=\frac{xb}{RT}\text{ (Given)}$$

$$\Rightarrow\quad x=1$$

09 A car tyre is filled with nitrogen gas at 35 psi at 27°C. It will burst if pressure exceeds 40 psi. The temperature in °C at which the car tyre will burst is ..... (Rounded-off to the nearest integer). **[2021, 25 Feb Shift-I]**

Ans. ***(70)***

$p_1=35\text{ psi}, T_1=27^\circ C=300\,K$

$p_2=40\text{ psi}, T_2=?$

According to Charle's law,

$$p\propto T$$

$$\frac{p_2}{p_1}=\frac{T_2}{T_1}\Rightarrow\frac{40}{35}=\frac{T_2}{300}$$

$$\Rightarrow\quad T_2=\frac{300\times40}{35}$$

$$=342.85\,K=69.7^\circ C$$

$$T_2\simeq70^\circ C$$

Hence, answer is 70.

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10 The volume occupied by 4.75 g of acetylene gas at 50°C and 740 mm Hg pressure is .....L (Rounded off to the nearest integer).

[Given, $R = 0.0821$ L atm K^{-1} mol^{-1}] **[2021, 24 Feb Shift-II]**

Ans. ***(5)***

Given, mass of $C_2H_2(g) = 4.75$ g

Molecular weight = 26 g/mol

Temperature = 50 + 273 = 323 K

Pressure = 740 torr/mm of Hg

$$\text{Pressure} = \frac{740}{760}\text{ atm}$$

$$R = 0.0821\text{ L atm mol}^{-1}\text{ K}^{-1}$$

Hence, no. of mole $n = \frac{4.75}{26}$ mol

Formula used, $pV = nRT$ (ideal gas)

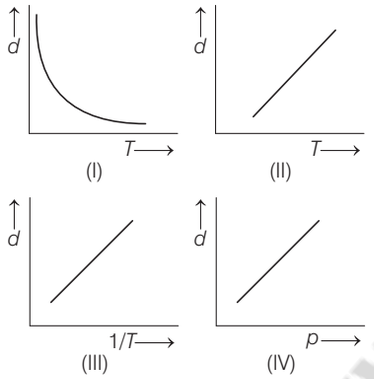
$$\Rightarrow V = \frac{nRT}{p}$$

$$= \frac{4.75}{26} \times \frac{0.0821 \times 323}{(740/760)}$$

$$= \frac{96314.078}{19240}$$

$$= 5.0059\text{ L} = 5\text{ L}$$

11 Which one of the following graphs is not correct for ideal gas? **[2020, 2 Sep Shift-I]**



d = density, p = pressure, T = temperature

(a) III (b) I

(c) IV (d) II

Ans. ***(d)***

Graph (II) is not correct for ideal gas.

For n mole of an ideal gas,

$$pV = nRT = \frac{w}{M}RT$$

$$\Rightarrow \quad p = \frac{w}{V} \times \frac{RT}{M} = d \times \frac{RT}{M}\left[\because \frac{w}{M} = d\right]$$

$$\Rightarrow \quad d = \frac{p \cdot M}{RT}$$

where, p = pressure, V = volume, T = temperature in K, R = molar gas constant, w = mass of the gas in g, M = gram molar mass of the gas and $d = \frac{w}{V}$ = density of the gas.

(i) When, p = constant $\Rightarrow d \propto \frac{1}{T}$

So, nature of the plot, d vs T is rectangular hyperbolic (I) but not linear (II).

Again, nature of the plot, d vs $\frac{1}{T}$ will be linear as in (III).

(ii) When, T = constant $\Rightarrow d \propto p$

Here, nature of the plot, d vs p will be linear as in (IV).

12 A mixture of one mole each of H_2, He and O_2 each are enclosed in a cylinder of volume, V at temperature T. If the partial pressure of H_2 is 2 atm, the total pressure of the gases in the cylinder is **[2020, 3 Sep Shift-II]**

(a) 14 atm (b) 38 atm

(c) 22 atm (d) 6 atm

Ans. ***(d)***

Volume of cylinder = V, Temperature = T,

Partial pressure of H_2 = 2 atm

According to law of partial pressure

$$p_i = \chi_i \times p_T$$

p_i = partial pressure of the ith component,

χ_i = mole fraction, p_T = total pressure

$$\Rightarrow \quad 2\text{ atm} = \left[\frac{n_{H_2}}{n_{H_2} + n_{He} + n_{O_2}}\right] \times p_T$$

Then, $p_T = 2 \times \frac{3}{1} = 6$ atm

13 For one mole of an ideal gas, which of these statements must be true?

(A) U and H each depends only on temperature.

(B) Compressibility factor Z is not equal to 1.

(C) $C_{p,m} - C_{V,m} = R$

(D) $dU = C_V dT$ for any process. **[2020, 4 Sep Shift-I]**

(a) (B), (C) and (D) (b) (A) and (C)

(c) (A), (C) and (D) (d) (C) and (D)

Ans. ***(c)***

Statements (A), (C) and (D) are true whereas (B) is false.

(A) For 1 mole, U = internal energy and H = enthalpy.

Heat capacity at constant volume.

$$nC_V = \frac{dU}{dt}$$

$$dU = nC_V dT \qquad (n = 1\text{ mol})$$

$$dU = 1 \times C_V \times dT \qquad (\because C_V = \text{constant})$$

$U = f(T)$ (Function of temperature)

U depends on temperature.

Heat capacity at constant volume,

$$nC_p = \frac{dH}{dT}$$

$$dH = nC_p dT \qquad [n = 1\text{ mol}]$$

$$dH = 1 \times C_p \times dT$$

In mathematically term,

$$H = f(T)\ [\because C_p = \text{constant}]$$

Hence, H depends on function of temperature

(b) Compressibility factor (Z) describe the deviation of real gas from ideal gas behaviour.

$$Z = \frac{pV}{RT} \qquad \ldots(i)$$

For ideal gas, $pV = nRT \qquad [n = 1\text{ mol}]$

$$pV = RT \qquad \ldots(ii)$$

Put in the value of pV from Eq. (ii) to Eq. (i)

$$Z = \frac{RT}{RT} = 1$$

Compressibility factor is 1 for ideal gas then option (b) is incorrect.

(c) For ideal gas,

$$C_p - C_V = nR \qquad (n = 1\text{ mol})$$

$$C_p - C_V = R$$

It is correct statement.

(d) $\Delta U = C_V dT \Rightarrow nC_V = \frac{dU}{dT}$

$$dU = nC_V dT \qquad (n = 1\text{ mol})$$

$$dU = C_V dT$$

It is also correct.

14 A spherical balloon of radius 3 cm containing helium gas has a pressure of 48×10^{-3} bar. At the same temperature, the pressure, of a spherical balloon of radius 12 cm containing the same amount of gas will be ..... $\times 10^{-6}$ bar. **[2020, 6 Sep Shift-I]**

Ans. ***(750)***

Initial pressure (p_1) = 48×10^{-3} bar

Final pressure (p_2) = ... $\times 10^{-6}$ bar

Initial volume (V_1) = $\frac{4}{3}\pi(3)^3$

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Final volume $(V_2) = \frac{4}{3}\pi(12)^3$

According to Boyle's law $p_1V_1 = p_2V_2$

$$p_2 = \frac{p_1V_1}{V_2} = \frac{48\times10^{-3}\times\frac{4}{3}\pi(3)^3}{\frac{4}{3}\pi(12)^3}$$

$$= \frac{48\times10^{-3}\times(3)^3}{(12)^3}$$

$$= \frac{48\times10^{-3}\times27}{1728} = 0.0277\times27\times10^{-3}$$

$$= 750\times10^{-6} \text{ bar}$$

Hence, the correct answer is 750.

15 The relative strength of interionic/ intermolecular forces in decreasing order is **[2020, 7 Jan Shift-I]**

(a) dipole-dipole > ion-dipole > ion-ion
(b) ion-ion > ion-dipole > dipole-dipole
(c) ion-dipole > ion-ion > dipole-dipole
(d) ion-dipole > dipole-dipole > ion-ion

Ans. ***(b)***

Interionic (ion-ion) forces are stronger than ion-dipole, which in turn are stronger than intermolecular forces like dipole-dipole interaction.

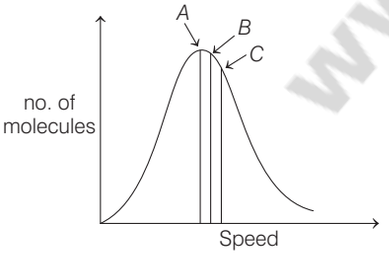
This is because in case of ion-ion interactions there is complete transfer of electrostatic charges from one atom to another. Whereas in dipole-dipole interactions, there is involvement of only partial charges.

The strength of ion-dipole interactions lies intermediate to that of ion-ion and dipole-dipole interactions.

Thus, the correct decreasing order of relative strength is :

Ion-ion > ion-dipole > dipole-dipole.

16 Identify the correct labels of *A*, *B* and *C* in the following graph from the options given below :



Root mean square speed (v_{rms}); most probable speed (v_{mp}); Average speed (v_{av}) **[2020, 7 Jan Shift-II]**

(a) A-v_{rms}; B-v_{mp}; C-v_{av}
(b) A-v_{mp}; B-v_{rms}; C-v_{av}
(c) A-v_{mp}; B -v_{av}; C-v_{rms}
(d) A-v_{av}; B-v_{rms}; C-v_{mp}

Ans. ***(c)***

The increasing order of molecular velocities of gas molecules is as follows :

Most probable velocity (v_{mp}) < average velocity (v_{av}) < rms velocity (v_{rms}).

Because,

$$v_{mp} = \sqrt{\frac{2RT}{M}},\ v_{av} = \sqrt{\frac{8RT}{\pi M}}$$

and $$v_{rms} = \sqrt{\frac{3RT}{M}}$$

17 Consider the van der Waals' constants, *a* and *b*, for the following gases.

Gas	Ar	Ne	Kr	Xe
a/(atm dm^6 mol^{-2})	1.3	0.2	5.1	4.1
b/(10^{-2} dm^3 mol^{-1})	3.2	1.7	1.0	5.0

Which gas is expected to have the highest critical temperature ? **[2019, 9 April Shift-I]**

(a) Kr (b) Xe (c) Ar (d) Ne

Ans. ***(a)***

Critical temperature is the temperature of a gas above which it cannot be liquefied what ever high the pressure may be. The kinetic energy of gas molecules above this temperature is sufficient enough to overcome the attractive forces. It is represented as T_c.

$$T_c = \frac{8a}{27Rb}$$

For Ar, $T_c = \frac{8\times1.3}{27\times8.314\times3.2} = 0.0144$

For Ne, $T_c = \frac{8\times0.2}{27\times8.314\times1.7} = 0.0041$

For Kr, $T_c = \frac{8\times5.1}{27\times8.314\times1.0} = 0.18$

For Xe, $T_c = \frac{8\times4.1}{27\times8.314\times5.0} = 0.02$

The value of T_c is highest for Kr (Krypton).

18 At a given temperature *T*, gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour. Their equation of state is given as,

$p = \frac{RT}{V-b}$ at *T*.

Here, *b* is the van der Waals' constant. Which gas will exhibit steepest increase in the plot of *Z* (compression factor) *vs p*? **[2019, 9 April Shift-II]**

(a) Xe (b) Ar (c) Kr (d) Ne

Ans. ***(a)***

Noble gases such as Ne, Ar, Xe and Kr found to deviate from ideal gas behaviour.

Xe gas will exhibit steepest increase in plot of *Z vs p*. Equation of state is given as:

$$p = \frac{RT}{(V-b)}$$

$$\Rightarrow \quad p(V-b) = RT$$

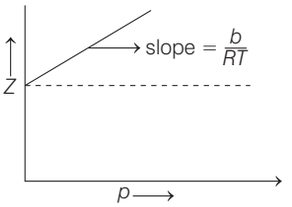
$$pV - pb = RT$$

$$\Rightarrow \quad pV = RT + pb$$

$$\frac{pV}{RT} = 1 + \frac{pb}{RT}.\ \text{As, } Z = \frac{pV}{RT}$$

so, $$Z = 1 + \frac{pb}{RT} \Rightarrow y = c + mx$$

The plot of *Z vs p* is found to be



The gas with high value of *b* will be steepest as slope is directly proportional to *b*. *b* is the van der Waals' constant and is equal to four times the actual volume of the gas molecules. Xe gas possess the largest atomic volume among the given noble gases (Ne, Kr, Ar). Hence, it gives the steepest increase in the plot of *Z* (compression factor) *vs p*.

19 Consider the following table.

Gas	*a*/(k Pa dm^{6}mol^{-1})	*b*/(dm^{3}mol^{-1})
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

a and *b* are van der Waals' constants. The correct statement about the gases is **[2019, 10 April Shift-I]**

(a) gas *C* will occupy lesser volume than gas *A*; gas *B* will be lesser compressible than gas *D*
(b) gas *C* will occupy more volume than gas *A*; gas *B* will be more compressible than gas *D*
(c) gas *C* will occupy more volume than gas *A*; gas *B* will be lesser compressible than gas *D*
(d) gas *C* will occupy more volume than gas *A*; gas *B* will be lesser compressible than gas *D*

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Ans. ***(b)***

For 1 mole of a real gas, the van der Waals' equation is

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT$$

The constant '*a*' measures the intermolecular force of attraction of gas molecules and the constant '*b*' measures the volume correction by gas molecules after a perfectly inelastic binary collision of gas molecules.

For gas *A* and gas *C* given value of '*b*' is $0.05196\ dm^3\ mol^{-1}$. Here,

$a \propto$ intermolecular force of attraction

$\propto$ compressibility $\propto$ real nature

$$\propto \frac{1}{\text{volume occupied}}$$

Value of $a/(kPa\ dm^6\ mol^{-1})$ for gas *A* (642.32) > gas *C* (431.91) So, gas *C* will occupy more volume than gas *A*. Similarly, for a given value of *a* say $155.21\ kPa\ dm^6\ mol^{-1}$ for gas *B* and gas *D*

$\frac{1}{b} \propto$ intermolecular force of attraction

$\propto$ compressibility $\propto$ real nature

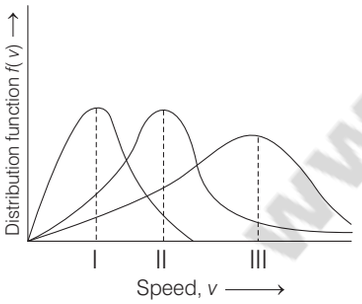
$$\propto \frac{1}{\text{volume accupied}}$$

$b/(dm^3\ mol^{-1})$ for gas *B* (0.04136) < Gas *D* (0.4382).

So, gas *B* will be more compressible than gas *D*.

20 Points I, II and III in the following plot respectively correspond to (v_{mp} : most probable velocity)

[2019, 10 April Shift-II]



(a) v_{mp} of H_2 (300 K); v_{mp} of N_2 (300 K); v_{mp} of O_2 (400 K)

(b) v_{mp} of O_2 (400 K); v_{mp} of N_2 (300 K); v_{mp} of H_2 (300 K)

(c) v_{mp} of N_2 (300 K); v_{mp} of O_2 (400 K); v_{mp} of H_2 (300 K)

(d) v_{mp} of N_2 (300 K); v_{mp} of H_2 (300 K); v_{mp} of O_2 (400 K)

Ans. ***(c)***

Key Idea From kinetic gas equation,

Most probable velocity $(v_{mp}) = \sqrt{\frac{2RT}{M}}$

where, R = gas constant,

T = temperature,

M = molecular mass

$$v_{mp} = \sqrt{\frac{2RT}{M}} \text{ i.e. } v_{mp} \propto \sqrt{\frac{T}{M}}$$

Gas	*M*	*T(K)*	$\sqrt{T/M}$
H_2	2	300	$\sqrt{300/2}=\sqrt{150}$ ...III (Highest)
N_2	28	300	$\sqrt{300/28}=\sqrt{10.71}$ ...I (Lowest)
O_2	32	400	$\sqrt{400/32}=\sqrt{12.5}$ ... II

So,

I. corresponds to v_{mp} of N_2 (300 K)

II. corresponds to v_{mp} of O_2 (400 K)

III. corresponds to v_{mp} of H_2 (300 K)

21 An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is

(a) 750 K (b) 500 K

(c) 750°C (d) 500°C

[2019, 12 Jan Shift-II]

Ans. ***(b)***

Given, temperature $(T_1) = 27°C$

$= 273 + 27 = 300\ K$

Volume of vessel = constant

Pressure in vessel = constant

Volume of air reduced by $\frac{2}{5}$ so the remaining volume of air is $\frac{3}{5}$.

Let at T_1 the volume of air inside the vessel is *n* so at T_2 the volume of air will be $\frac{3}{5}n$.

Now, as *p* and *V* are constant, so

$$n \cdot T_1 = \frac{3}{5} n T_2 \qquad ...(i)$$

Putting the value of T_1 in equation (i) we get,

$$n \times 300 = \frac{3}{5} n \times T_2$$

or $$T_2 = 300 \times \frac{5}{3} = 500\ K$$

22 The volume of gas *A* is twice than that of gas *B*. The compressibility factor of gas *A* is thrice than that of gas *B* at same temperature. The pressures of the gases for equal number of moles are

[2019, 12 Jan Shift-I]

(a) $p_A = 2p_B$ (b) $2p_A = 3p_B$

(c) $p_A = 3p_B$ (d) $3p_A = 2p_B$

Ans. ***(b)***

Given, $Z_A = 3Z_B$

Compressibility factor $(Z) = \frac{pV}{nRT}$

[for real gases]

On substituting in equation (i), we get

$$\frac{p_A V_A}{n_A R T_A} = \frac{3p_B V_B}{n_B R T_B} \qquad ...(ii)$$

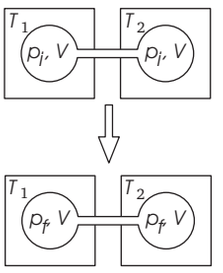
Also, it is given that

$$V_A = 2V_B,\ n_A = n_B \text{ and } T_A = T_B$$

$\therefore$ Eq. (ii) becomes

$$\frac{p_A \times 2V_B}{n_B R T_B} = \frac{3p_B V_B}{n_B R T_B} \Rightarrow 2p_A = 3p_B$$

23 Two closed bulbs of equal volume (*V*) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2. The final pressure p_f is **[JEE Main 2016]**



(a) $2p_i\left(\frac{T_1}{T_1+T_2}\right)$ (b) $2p_i\left(\frac{T_2}{T_1+T_2}\right)$

(c) $2p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$ (d) $p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$

Ans. ***(b)***

Initially,

Number of moles of gases in each container $= \frac{p_i V}{RT_1}$

Total number of moles of gases in both containers

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$$= 2\frac{p_i V}{RT_1}$$

After mixing, number of moles in left chamber

$$= \frac{p_f V}{RT_1}$$

Number of moles in right chamber $= \frac{p_f V}{RT_2}$

Total number of moles

$$= \frac{p_f V}{RT_1} + \frac{p_f V}{RT_2}$$

$$= \frac{p_f V}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$$

As total number of moles remains constant.

Hence, $\frac{2p_i V}{RT_1} = \frac{p_f V}{RT_1} + \frac{p_f V}{RT_2}$

$\Rightarrow$ $p_f = 2p_i\left(\frac{T_2}{T_1 + T_2}\right)$

24 The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is **[JEE Main 2015]**

(a) ion-ion interaction
(b) ion-dipole interaction
(c) London force
(d) hydrogen bond

Ans. ***(b)***

Ion-ion interaction is dependent on the square of distance, i.e. ion-ion

interaction $\propto \frac{1}{r^2}$

Similarly, ion-dipole interaction $\propto \frac{1}{r^3}$

London forces $\propto \frac{1}{r^6}$

and dipole-dipole interactions $\propto \frac{1}{r^3}$

Superficially it seems as both ion dipole interaction and hydrogen bonding vary with the inverse cube of distance between the molecules but when we look at the exact expressions of field (force) created in two situations it comes as

$$|\mathbf{E}| \text{ or } |\mathbf{F}| = \frac{2|\mathbf{P}|}{4\pi\varepsilon_0 r^3}$$

(In case of ion-dipole interaction)

and $$F = \frac{2q^2 r - 4q^2 a}{4\pi\varepsilon_0 r^3}$$

(In case of dipole-dipole interaction)
From the above it is very clear, the ion-dipole interaction is the better answer as compared to dipole-dipole interaction i.e. hydrogen bonding.

25 If Z is a compressibility factor, van der Waals' equation at low pressure can be written as **[JEE Main 2014]**

(a) $Z = 1 + \frac{RT}{pb}$
(b) $Z = 1 - \frac{a}{VRT}$
(c) $Z = 1 - \frac{pb}{RT}$
(d) $Z = 1 + \frac{pb}{RT}$

Ans. ***(b)***

van der Waals' equation is given by

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

At low pressure, V decreases. Thus, $\frac{a}{V^2}$ increases. However, V is still large enough in comparison to 'b', hence, 'b' can be neglected. Thus, van der Waals' equation becomes

$$\left(p + \frac{a}{V^2}\right)V = RT$$

$\Rightarrow$ $pV + \frac{a}{V} = RT$

$\Rightarrow$ $pV = RT - \frac{a}{V}$

$\Rightarrow$ $\frac{pV}{RT} = 1 - \frac{a}{RTV}$

$$Z = 1 - \frac{a}{RTV} \quad \left[\because \frac{pV}{RT} = Z\right]$$

26 For gaseous state, if most probable speed is denoted by C^*, average speed by $\overline{C}$ and mean square speed by C, then for a large number of molecules, the ratios of these speeds are **[JEE Main 2013]**

(a) $C^* : \overline{C} : C = 1.225 : 1.128 : 1$
(b) $C^* : \overline{C} : C = 1.128 : 1.225 : 1$
(c) $C^* : \overline{C} : C = 1 : 1.128 : 1.225$
(d) $C^* : \overline{C} : C = 1 : 1.225 : 1.128$

Ans. ***(c)***

C^* = most probable speed $= \sqrt{2RT/M}$

$\overline{C}$ = average speed $= \sqrt{8RT/\pi M}$

C = Mean square speed corrected as

$$\text{rms} = \sqrt{\frac{3RT}{M}}$$

$\therefore$ $C^* < \overline{C} < C$

Hence, $C^* : \overline{C} : C = 1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}}$

$= 1 : 1.128 : 1.225$

Note As no option correspond to mean square speed, it is understood as misprint. It should be root mean square speed.

27 The compressibility factor for a real gas at high pressure is **[AIEEE 2012]**

(a) $1 + \frac{RT}{pb}$ (b) 1

(c) $1 + \frac{pb}{RT}$ (d) $1 - \frac{pb}{RT}$

Ans. ***(c)***

van der Waals' equation for one mole of real gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

When pressure is high $p >> \frac{a}{V^2}$

Such that $\left(p + \frac{a}{V^2}\right) \approx p$

Thus, $p(V - b) = RT$

$pV - pb = RT$

$pV = RT + pb$

$\therefore$ Compressibility factor,

$$Z = \frac{pV}{RT} = \left(1 + \frac{pb}{RT}\right)$$

28 a and b are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because **[AIEEE 2011]**

(a) a and b for $Cl_2 > a$ and b for C_2H_6
(b) a and b for $Cl_2 < a$ and b for C_2H_6
(c) a for $Cl_2 > a$ for C_2H_6 but b for $Cl_2 > b$ for C_2H_6
(d) a for $Cl_2 > a$ for C_2H_6 but b for $Cl_2 < b$ for C_2H_6

Ans. ***(d)***

van der Waals' constant a is due to force of attraction and b due to finite size of molecules.

Thus, greater the value a and smaller the value of b, larger the liquefaction.

Thus, $a(Cl_2) > a(C_2H_6)$

and $b(Cl_2) < b(C_2H_6)$

29 The molecular velocity of any gas is **[AIEEE 2011]**

(a) inversely proportional to the square root of temperature
(b) inversely proportional to absolute temperature
(c) directly proportional to square of temperature
(d) directly proportional to square root of temperature

Ans. ***(d)***

Molecular velocity can be

$$\text{average velocity} = \frac{\sqrt{8RT}}{\pi M}$$

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root mean square velocity $= \sqrt{\frac{3RT}{M}}$

most probable velocity $= \sqrt{\frac{2RT}{M}}$

In all cases, molecular velocity $\propto \sqrt{T}$

30 When r, p and M represent rate of diffusion, pressure and molecular mass, respectively, then the ratio of the rates of diffusion (r_A / r_B) of two gases A and B, is given as **[AIEEE 2011]**

(a) $(p_A / p_B)^{1/2}(M_A / M_B)$
(b) $(p_A / p_B)(M_B / M_A)^{1/2}$
(c) $(p_A / p_B)^{1/2}(M_B / M_A)$
(d) $(p_A / p_B)(M_A / M_B)^{1/2}$

Ans. ***(b)***

Rate of diffusion, $r \propto p$

$$r = \frac{1}{\sqrt{M}} \therefore r \propto \frac{p}{\sqrt{M}}$$

For gas A, $r_A \propto \frac{p_A}{\sqrt{M_A}}$ ...(i)

For gas B, $r_B \propto \frac{p_B}{\sqrt{M_B}}$ ...(ii)

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{r_A}{r_B} = \frac{p_A}{p_B}\cdot\sqrt{\frac{M_B}{M_A}} \text{ or } = \frac{p_A}{p_B}\left(\frac{M_B}{M_A}\right)^{1/2}$$

31 If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, then how many moles of water are in the vapour phase when equilibrium is established?
(Given, vapour pressure of H_2O at 300 K is 3170 Pa;
$R = 8.314$ JK^{-1} mol^{-1}) **[AIEEE 2010]**

(a) 5.56×10^{-3} mol (b) 1.53×10^{-2} mol
(c) 4.46×10^{-2} mol (d) 1.27×10^{-3} mol

Ans. ***(d)***

Number of moles,

$$n = \frac{pV}{RT} = \frac{3170 \times 10^{-3}}{8.134 \times 300}$$

$$= 1.27 \times 10^{-3} \text{ mol}$$

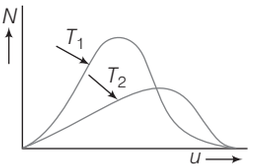
32 Which one of the following statements is not true about the effect of an increase in temperature on the distribution of molecular speeds in a gas? **[AIEEE 2005]**

(a) The area under the distribution curve remains the same as under the lower temperature
(b) The distribution becomes broader
(c) The fraction of the molecules with the most probable speed increases
(d) The most probable speed increases

Ans. ***(c)***

Distribution of molecules (N) with velocity (u) at two temperatures T_1 and T_2 ($T_2 > T_1$) is shown below

At both temperatures, distribution of molecules with increase in velocity first increases, reaches to a maximum value and then decreases.



33 As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of which of the following? **[AIEEE 2004]**

(a) 1/2 (b) $\sqrt{313/293}$
(c) 313/293 (d) 2

Ans. ***(c)***

$$\text{Average KE} = \frac{3}{2}RT/N_0$$

$$\Rightarrow \quad (\text{KE}) \propto T$$

$$\therefore \quad (\text{KE})_{313}/(\text{KE})_{293} = \frac{313}{293}$$

34 In van der Waals' equation of state of the gas law, the constant 'b' is a measure of **[AIEEE 2004]**

(a) intermolecular repulsions
(b) intermolecular attraction
(c) volume occupied by the molecules
(d) intermolecular collisions per unit volume

Ans. ***(c)***

van der Waals' equation for one mole of a gas is

$$\left[p + \frac{a}{V^2}\right][V - b] = RT$$

where, b is volume correction. It arises due to finite size of molecules.

35 According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels **[AIEEE 2003]**

(a) in a circular path
(b) in a wavy path
(c) in a straight line path
(d) with an accelerated velocity

Ans. ***(c)***

In between two successive collisions, no force is acting on the gas molecules. Resultantly they travel with uniform velocity during this interval and hence, moves along a straight line.

36 Based on kinetic theory of gases following laws can be proved **[AIEEE 2002]**

(a) Boyle's law
(b) Charles' law
(c) Avogadro's law
(d) All of these

Ans. ***(d)***

On the basis of kinetic theory of gases

$$pV = \frac{1}{3}Nm\bar{v}^2$$

and $$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT$$

$$p = \frac{1}{3}\left(\frac{N}{V}\right)m\bar{v}^2$$

or $$p = \frac{2}{3}\left(\frac{N}{V}\right)\frac{1}{2}m\bar{v}^2$$

$$= \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{3}{2}\right)kT$$

or $$pV = NkT$$

37 For an ideal gas, number of moles per litre in terms of its pressure p, temperature T and gas constant R is **[AIEEE 2002]**

(a) $\frac{pT}{R}$ (b) pRT
(c) $\frac{p}{RT}$ (d) $\frac{RT}{p}$

Ans. ***(c)***

According to ideal gas equation,
$pV = nRT$

Number of moles, $n = \frac{pV}{RT} = \frac{p \times 1}{RT} = \frac{p}{RT}$

TOPIC 2
Liquid State

38 The predominant intermolecular forces present in ethyl acetate, a liquid, are : **[2020, 8 Jan Shift-I]**

(a) London dispersion and dipole-dipole
(b) London dispersion, dipole-dipole and hydrogen bonding
(c) Dipole-dipole and hydrogen bonding
(d) Hydrogen bonding and London dispersion

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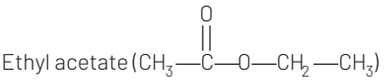
Ans. ***(a)***



Ethyl acetate ($CH_3—\overset{\overset{O}{\|}}{C}—O—CH_2—CH_3$) molecules are polar. So, dipole-dipole interaction is present between its molecules. There are no such groups such as hydroxyl (—OH) which are capable of forming hydrogen bond.

London dispersion forces are present in all substances involving ethyl acetate also.

Thus in ethyl acetate, the predominant intermolecular forces are London dispersion and dipole-dipole forces.

TOPIC 3
Solid State

38 The empirical formula for a compound with a cubic close packed arrangement of anions and with cations occupying all the octahedral sites in A_xB. The value of x is ..... (Integer answer)

[2021, 31 Aug Shift-II]

Ans. ***(1)***

In A_xB,

Effective number of B atom = 4 (in ccp)

Effective number of A atom = 4 (octahedral void)

So, formula of compound = $A_4B_4 \Rightarrow AB$

$\therefore \quad x = 1$

40 Match List-I with List-II.

	List-I (Property)		List-II (Example)
A.	Diamagnetism	1.	MnO
B.	Ferrimagnetism	2.	O_2
C.	Paramagnetism	3.	NaCl
D.	Antiferromagnetism	4.	Fe_3O_4

Choose the most appropriate answer from the options given below. **[2021, 27 Aug Shift-I]**

	A	B	C	D
(a)	2	1	3	4
(b)	1	3	4	2
(c)	3	4	2	1
(d)	4	2	1	3

Ans. ***(c)***

A. NaCl is diamagnetic because all electrons are paired in Na^+ and in Cl^-. So, it shows diamagnetism.

B. Fe_3O_4 is ferrimagnetic because of the presence of the unequal alignment of magnetic moment in opposite direction.

C. O_2 molecule has two unpaired electrons. So, it is paramagnetic.

D. In MnO, the orientation of the electrons of Mn and O is such that they cancel their effects, hence it is antiferromagnetic.

So, the correct match is A-3, B-4, C-2, D-1.

41 Select the correct statements.

(A) Crystalline solids have long range order.

(B) Crystalline solids are isotropic.

(C) Amorphous solids are sometimes called pseudo solids.

(D) Amorphous solids soften over a range of temperatures.

(E) Amorphous solids have a definite heat of fusion.

Choose the most appropriate answer from the options given below. **[2021, 27 July Shift-II]**

(a) (A), (B), (E) only

(b) (B), (D) only

(c) (C), (D) only

(d) (A), (C), (D) only

Ans. ***(d)***

Statements (A), (C), (D) are correct whereas (B) and (E) are incorrect.

(A) Crystalline solids have definate arrangement of constituent particles. Hence, they have long range order.

(B) Crystalline solids are anisotropic, i.e. some of its physical properties (like electrical resistance or refractive index) show different values when measured along different directions in the same crystal.

(C) Amorphous solids are highly supercooled liquids of very high viscosity thats why they are sometimes called pseudo solids.

(D) Amorphous solids tend to soften slowly over a wide temperature range rather than having a well defined melting point.

(E) Since, they melt over a range of temperature and start to flow without completely changing into liquid. Therefore, they do not have definite heat of fusion.

42 The parameters of the unit cell of a substance are $a = 2.5, b = 3.0, c = 4.0$, $\alpha = 90°, \beta = 120°, \gamma = 90°$. The crystal system of the substance is

[2021, 27 July Shift-I]

(a) hexagonal (b) orthorhombic

(c) monoclinic (d) triclinic

Ans. ***(c)***

The parameters of unit cell of a substance are

$a = 2.5, b = 3.0, c = 4.0$

that means $a \neq b \neq c$

$\alpha = 90°, \beta = 120°, \gamma = 90°$

$\therefore \quad \alpha = \gamma = 90°$

$\beta = 120°$

(a) For hexagonal crystal, $a = b \neq c$

$\alpha = \beta = 90°$

$\gamma = 120°$

(b) Orthorhombic crystal, $a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

(c) Monoclinic crystal, $a \neq b \neq c$

$\alpha = \gamma = 90°$

$\beta \neq 90°$

(d) Triclinic crystal, $a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$

Therefore, given parameters of unit cell is of monoclinic crystal.

43 Given below are two statements.

Statement I Frenkel defects are vacancy as well as interstitial defects.

Statement II Frenkel defect leads to colour in ionic solids due to presence of F-centres.

Choose the most appropriate answer for the statements from the options given below.

[2021, 26 Aug Shift-I]

(a) Statement I is false but Statement II is true.

(b) Both statement I and statement II are true.

(c) Statement I is true but statement II is false.

(d) Both Statement I and statement II are false.

Ans. ***(c)***

Frenkel defect is vacancy as well as interstitial defect as atom leaves its place in lattice creating a vacancy and occupy interstitial site in a nearby location. Hence, statement I is true.

Frenkel defect does not leads to colour in ionic solids due to absence of

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F-centres. Ionic solids having anionic vacancies because of metal excess defects. This leads to colour in ionic solids due to presence of F-centres. Hence, statement II is false.

44 A copper complex crystallising in a ccp lattice with a cell edge of 0.4518 nm has been revealed by employing X-ray diffraction studies. The density of a copper complex is found to be 7.62 g cm^{-3}. The molar mass of copper complex is ..... g mol^{-1}. (Nearest integer)
[Given : $N_A = 6.022 \times 10^{23}\ mol^{-1}$]
[2021, 22 July Shift-II]

Ans. ***(106)***

Edge length, $a = 0.4518$ nm
Density, $d = 7.62\ g/cm^3$
Using formula of density,

$$d = \frac{Z \times M}{N_A \times V}$$

Here, Z = Number of atom per unit cell i.e. for ccp = 4
M = Molar mass of copper complex = ?
N_A = Avogadro number i.e. $6.023 \times 10^{23}\ mol^{-1}$
V = Volume of unit cell.

$$\Rightarrow M = \frac{7.62\ g/cm^3 \times 6.022 \times 10^{23} mol^{-1} \times (0.4518 \times 10^{-7}\ cm)^3}{4}$$

$$= 105.79\ g/mol \simeq 106\ g\ mol^{-1}$$

45 Diamond has a three dimensional structure of C atoms formed by covalent bonds. The structure of diamond has face centred cubic lattice, where 50% of the tetrahedral voids are also occupied by carbon atoms. The number of carbon atoms present per unit cell of diamond is ..... .
[2021, 20 July Shift-II]

Ans. ***(8)***

Carbon atom in diamond occupy fcc lattice points as well as half of the tetrahedral voids.
Number of lattice point in fcc = 4
Number of tetrahedral voids = $2 \times 4 = 8$
$\therefore$ 50% of tetrahedral voids = $8/4 \times 2$
Effective number of atoms of carbon

$$= 4 + 8 \times \frac{1}{2} = 8$$

46 In a binary compound, atoms of element A form a hcp structure and those of element M occupy 2/3 of the tetrahedral voids of the hcp structure. The formula of the binary compound is
[2021, 18 Mar Shift-I]
(a) M_2A_3 (b) M_4A_3 (c) M_4A (d) MA_3

Ans. ***(b)***

For HCP unit cell,
Number of atom per unit cell $Z = 6$, so $A = 6$
Also, we know
If $Z = 6$, so the number of tetrahedral voids = 2×6
Now, if 2/3 of these voids are occupied by M the number of $M = \frac{2}{3} \times 2 \times 6 = 8$
$\therefore$ Formula = $M_8A_6 = M_4A_3$

47 KBr is doped with 10^{-5} mole per cent of $SrBr_2$. The number of cationic vacancies in 1 g of KBr crystal is ..... 10^{14} (Round off to the nearest integer).
[Atomic mass : K = 39.1 u, Br = 79.9 u, $N_A = 6.023 \times 10^{23}$]
[2021, 17 March Shift-II]

Ans. ***(5)***

The number of cationic vacancies in 1 g of KBr crystal is 5×10^{14}.
For every Sr^{2+} ion, 1 cationic vacancy is created. Hence, number of Sr^{2+} ion = number of cationic vacancies
Since, the mole percentage of $SrBr_2$ dopped is 10^{-5} to that of total moles of KBr.
Hence, number of cationic vacancy

$$= \frac{10^{-5}}{100} \times \frac{1}{119} \times N_A$$

$$= \frac{1}{119} \times 10^{-7} \times 6.022 \times 10^{23}$$

(Mass of KBr = 119)

$$= 5 \times 10^{-2} \times 10^{-7} \times 10^{23} = 5 \times 10^{14}$$

48 Ga (atomic mass 70 u) crystallises in a hexagonal close packed structure. The total number of voids in 0.581 g of Ga is ..... $\times 10^{21}$. (Round off to the nearest integer).
[2021, 16 March Shift-II]

Ans. ***(15)***

For HCP structure,
Effective number of atoms per unit cell (Z) = 6
Number of tetrahedral void = $2Z = 12$
Number of octahedral void = $Z = 6$
Total number of voids per unit cell = 18

$$\text{Moles of Ga} = \frac{\text{Given mass}}{\text{Molar mass}} = \frac{0.581}{70}$$

$$\text{No. of atoms} = \frac{0.581}{70} \times N_A$$

$$\text{No. of unit cells} = \frac{0.581}{70} \times \frac{N_A}{6}$$

$$\text{No. of voids} = \left(\frac{0.581}{70} \times \frac{6.02 \times 10^{23}}{6}\right) \times 18$$

$$= 14.99 \times 10^{21}.$$

Nearest integer = 15×10^{21}
So, correct answer is 15.

49 The number of octahedral voids per lattice site in a lattice is ..... . (Rounded off to the nearest integer)
[2021, 26 Feb Shift-II]

Ans. ***(1)***

Let us assume, the crystal has fcc or ccp lattice which has octahedral voids.
Number of lattice sites occupied = 8 corner + 6 face centres = 14
Number of octahedral voids = 12 edge centres + 1 body centre = 13
Number of octahderal void (s) per lattice site

$$= \frac{13}{14} = 0.928 \simeq 1$$

50 The unit cell of copper corresponds to a face centered cube of edge length 3.596 Å with one copper atom at each lattice point. The calculated density of copper in kg/m^3 is ..... . [Molar mass of Cu = 63.54 g ; Avogadro number = 6.022×10^{23}]
[2021, 25 Feb Shift-II]

Ans. ***(9077)***

Density of copper, $d = \frac{Z \times M}{a^3 \times N_A}$

Given, $Z = 4$, for fcc lattice,
$M = 63.54\ g\ mol^{-1}$
$= 63.54 \times 10^{-3}\ kg\ mol^{-1}$,
$a = 3.596\ Å = 3.596 \times 10^{-10}$ m,
$N_A = 6.022 \times 10^{23}\ mol^{-1}$
On putting given values, we get

$$\Rightarrow d = \frac{4 \times (63.54 \times 10^{-3})}{(3.596 \times 10^{-10})^3 \times (6.022 \times 10^{23})}\ kg/m^3$$

$$= 9076.26 \simeq 9077\ kg/m^3$$

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51 The coordination number of an atom in a body centered cubic structure is ..... .

[Assume that the lattice is made up of atoms.] **[2021, 24 Feb Shift-I]**

Ans. ***(8)***

Coordination number is the number of nearest neighbours of a central atom in the structure.

bcc has a coordination number of 8 and contains 2 atoms per unit cell.

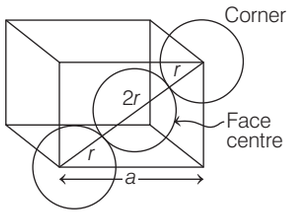
This is because each atom touches four atoms in the layer above it, four in the layer below it and none in its own layer.

52 An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^{3} kg m^{-3}, the radius of the element is approximately ..... $\times10^{-12}$ m (to the nearest integer).

[2020, 3 Sep Shift-I]

Ans. ***(143.00)***

For the cubic ($Z=4$) unit cell,



r = Radius of the element

a = Edge length of the cubic unit cell (fcc) = 405 pm

$$4r=\sqrt{2}a \Rightarrow r=\frac{\sqrt{2}\times405}{4}\text{ pm}$$

$$=143.189\text{ pm}\simeq143\text{ pm}=143\times10^{-12}\text{ m}$$

53 A diatomic molecule X_2 has a body-centred cubic (bcc) structure with a cell edge of 300 pm. The density of the molecule is 6.17 g cm^{-3}. The number of molecules present in 200 g of X_2 is (Avogadro constant $(N_A)=6\times10^{23}$ mol^{-1})

[2020, 5 Sep Shift-I]

(a) $40N_A$ (b) $2N_A$ (c) $8N_A$ (d) $4N_A$

Ans. ***(d)***

We know that, $d=\dfrac{Z\times M}{a^3\times N_A}$

Given, density $d=6.17$ g,

edge length $a=300\text{ pm}=3\times10^{-8}$ cm,

$N_A=6\times10^{23}$ mol^{-1}

$$\therefore\ 6.17=\frac{2\times M}{(3\times10^{-8})^3\times6\times10^{23}}$$

(For bcc, $Z=2$)

$\Rightarrow\ M=50$ g / mol

Hence, number of molecules present in 200 g of X_2 is

$$N=\frac{w}{M}\times N_A=\frac{200}{50}\times N_A=4N_A$$

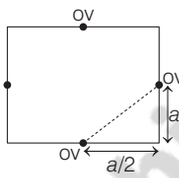
54 An element crystallises in a face-centred cubic (fcc) unit cell with cell edge a. The distance between the centres of two nearest octahedral voids in the crystal lattice is

[2020, 5 Sep Shift-II]

(a) $\dfrac{a}{\sqrt{2}}$ (b) a

(c) $\sqrt{2}a$ (d) $\dfrac{a}{2}$

Ans. ***(a)***



In fcc octahedral voids are present at the edge centers at body center.

Minimum distance between centers of two octohedral voids.

$$x=\sqrt{\left(\frac{a}{2}\right)^2+\left(\frac{a}{2}\right)^2}=\sqrt{\frac{a^2}{4}+\frac{a^2}{4}}=\frac{a}{\sqrt{2}}$$

55 A crystal is made up of metal ions M_1 and M_2 and oxide ions. Oxide ions form a ccp lattice structure. The cation M_1 occupies 50% of octahedral voids and the cation M_2 occupies 12.5% of tetrahedral voids of oxide lattice. The oxidation numbers of M_1 and M_2 are, respectively **[2020, 6 Sep Shift-II]**

(a) +2, +4 (b) +1, +3

(c) +3, +1 (d) +4, +2

Ans. ***(a)***

Number of O^{2-} ions in ccp = 4

Total charge on oxide = − 8

Number of tetrahedral voids = 8

Number of voids = 4

Number of cation M_1 occupies 50% of octahedral voids,

$$\frac{50}{100}\times4=2$$

Number of cation M_2 occupies 12.5% of tetrahedral voids of oxide lattice,

$$\frac{12.5}{100}\times8=1$$

So, formula is $(M_1)_2(M_2)O_4$.

This must be neutral. Both metals must have + 8 charge on total.

From given options :

$$\begin{cases}\text{Oxidaion number of}\quad M_1=+2\\ \text{Oxidaion number of}\quad M_2=+4\end{cases}$$

$\therefore\quad (2\times+2)+(1\times+4)=+8$

Hence, correct option is (a).

56 Which of the following compounds is likely to show both Frenkel and Schottky defects in its crystalline form? **[2020, 8 Jan Shift-II]**

(a) AgBr (b) CsCl

(c) KBr (d) ZnS

Ans. ***(a)***

AgBr shows both Schottky and Frenkel defects. Because the $\frac{r_+}{r_-}$ (radius of cation and radius of anion) ratio in AgBr is not very large or not very small.

(AgCl shows only Schottky defect due to greater value of $\frac{r_+}{r_-}$, whereas AgI shows only Frenkel defect due to smaller value of $\frac{r_+}{r_-}$).

57 Element '*B*' forms ccp structure and '*A*' occupies half of the octahedral voids, while oxygen atoms occupy all the tetrahedral voids. The structure of bimetallic oxide is **[2019, 8 April Shift-I]**

(a) A_2BO_4 (b) AB_2O_4 (c) A_2B_2O (d) A_4B_2O

Ans. ***(b)***

The number of element '*B*' in the crystal structure

= 4 *N*

Number of tetrahedral voids = 2*N*

Number of octahedral voids = *N*

$\therefore$ Number of '*A*' in the crystal $=\dfrac{N}{2}=\dfrac{4}{2}=2$

Number of oxygen (O) atoms

$=2N=2\times4=8$

$\therefore$ The structure of bimetallic oxide

$=A_2\ B_4\ O_8=AB_2\ O_4$

58 Consider the bcc unit cells of the solids 1 and 2 with the position of atoms as shown below. The radius of atom *B* is twice that of atom *A*.

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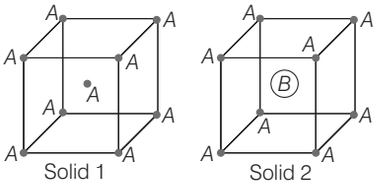
The unit cell edge length is 50% more is solid 2 than in 1. What is the approximate packing efficiency in solid 2?



(a) 65% (b) 90% (c) 75% (d) 45%

[2019, 8 April Shift-II]

Ans. ***(b)***

Key Idea Packing efficiency

$$= \frac{\text{Volume occupied by sphere}}{\text{Volume of cube}} \times 100$$

Given, $r_B = 2r_A$; $a_2 = a_1 + \frac{50}{100}a_1 = 1.5\,a_1$

For bcc lattice

$$4r_A = \sqrt{3}\,a_1$$

$$\Rightarrow \quad r_A = \frac{\sqrt{3}\,a_1}{4} \Rightarrow a_1 = \frac{4r_A}{\sqrt{3}}$$

$$\therefore \quad a_2 = 1.5\left(\frac{4r_A}{\sqrt{3}}\right) = \frac{3}{2}\left(\frac{4r_A}{\sqrt{3}}\right)$$

$$a_2 = 2\sqrt{3}\,r_A$$

Packing efficiency

$$= \frac{\frac{4}{3}\pi r_A^3 \times z_A + \frac{4}{3}\pi r_B^3 \times z_B}{a_2^3}$$

[As the atoms A are present at the edges only $z_A = \frac{1}{8} \times 8 = 1$, atom B is present only at the body centre $z_B = 1$]

$$\therefore \quad \text{PE}_2 = \frac{\left(\frac{4}{3}\pi r_A^3 \times 1\right) + \left(\frac{4}{3}\pi r_B^3 \times 1\right)}{a_2^3}$$

$$= \frac{\frac{4}{3}\pi r_A^3 + \frac{4}{3}\pi (2r_A)^3}{(2\sqrt{3}\,r_A)^3}$$

$$= \frac{\frac{4}{3}\pi r_A^3 \times 9}{8 \times 3\sqrt{3}\,r_A^3}$$

$$= \frac{\pi}{2\sqrt{3}} = 90.72\% \approx 90\%$$

59 10 mL of 1 mM surfactant solution forms a monolayer covering 0.24 cm^2 on a polar substrate. If the polar head is approximated as a cube, what is its edge length?

[2019, 9 April Shift-II]

(a) 2.0 pm (b) 0.1 nm
(c) 1.0 pm (d) 2.0 nm

Ans. ***(a)***

Given, volume

$= 10$ mL, Molarity $= 1$ mM $= 10^{-3}$ M

$\therefore$ Number of millimoles

$= 10\text{ mL} \times 10^{-3}\text{ M} = 10^{-2}$

Number of moles $= 10^{-5}$

Now, number of molecules

= Number of moles × Avogadro's number

$= 10^{-5} \times 6 \times 10^{23} = 6 \times 10^{18}$

Surface area occupied by 6×10^{18} molecules $= 0.24\ cm^2$

$\therefore$ Surface area occupied by 1 molecule

$$= \frac{0.24}{6 \times 10^{18}} = 0.04 \times 10^{-18}\ cm^2$$

As it is given that polar head is approximated as cube. Thus, surface area of cube $= a^2$,

where, a = edge length

$\Rightarrow \quad a^2 = 4 \times 10^{-20}\ cm^2$

$a = 2 \times 10^{-10}$ cm $= 2$ pm

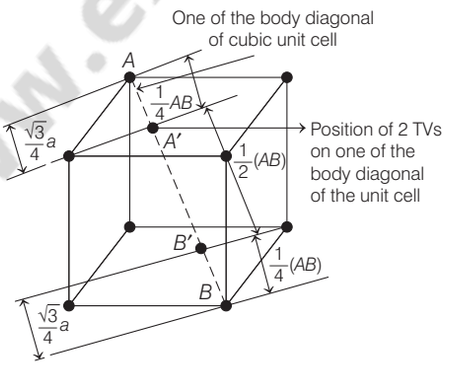
60 An element has a face-centred cubic (fcc) structure with a cell edge of a. The distance between the centres of two nearest tetrahedral voids in the lattice is

[2019, 12 April Shift-I]

(a) $\sqrt{2}a$ (b) a (c) $\frac{a}{2}$ (d) $\frac{3}{2}a$

Ans. ***(c)***

In fcc unit cell, two tetrahedral voids are formed on each of the four non-parallel body diagonals of the cube at a distance of $\sqrt{3}a/4$ from every corner along the body diagonal.



The angle between body diagonal and an edge is $\cos^{-1}(1/\sqrt{3})$. So, the projection of the line on an edge is $a/4$.

Similarly, other tetrahedral void also will be $a/4$ away.

So, the distance between these two is

$$\left[a - \frac{a}{4}\right] - \frac{a}{4} - \frac{a}{4} = \frac{a}{2}.$$

61 The ratio of number of atoms present in a simple cubic, body centered cubic and face centered cubic structure are, respectively.

[2019, 12 April Shift-II]

(a) 8 : 1 : 6 (b) 1 : 2 : 4
(c) 4 : 2 : 1 (d) 4 : 2 : 3

Ans. ***(b)***

The ratio of number of atoms present in simple cubic, body centred cubic and face centered cubic structure are 1 : 2 : 4 respectively.

62 At 100°C, copper (Cu) has FCC unit cell structure with cell edge length of x Å. What is the approximate density of Cu (in g cm^{-3}) at this temperature?

[Atomic mass of Cu = 63.55 u]

[2019, 9 Jan Shift-II]

(a) $\frac{211}{x^3}$ (b) $\frac{205}{x^3}$ (c) $\frac{105}{x^3}$ (d) $\frac{422}{x^3}$

Ans. ***(d)***

For fcc, rank of the unit cell $(Z) = 4$

Mass of one Cu-atom, $M = 63.55$ u

Avogadro's number,

$$N_A = 6.023 \times 10^{23}\text{ atom}$$

Edge length, $a = x\,\text{Å} = x \times 10^{-8}$ cm

$$\text{density}(d) = \frac{Z \times M}{N_A \times a^3}$$

$$= \frac{4 \times 63.55}{6.023 \times 10^{23} \times (x \times 10^{-8})^3}$$

$$= \frac{422.048}{x^3}\ \text{g cm}^{-3}$$

63 Which primitive unit cell has unequal edge lengths ($a \neq b \neq c$) and all axial angles different from 90°?

[2019, 10 Jan Shift-I]

(a) Hexagonal (b) Monoclinic
(c) Tetragonal (d) Triclinic

Ans. ***(d)***

Triclinic primitive unit cell has dimensions as, $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$.

Among the seven basic or primitive crystalline systems, the triclinic system is most unsymmetrical. In other cases, edge length and axial angles are given as follows :

Hexagonal : $a = b \neq c$

and $\alpha = \beta = 90°, \gamma = 120°$

Monoclinic : $a \neq b \neq c$

and $\alpha = \gamma = 90°, \beta \neq 90°$

Tetragonal : $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$

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64 A compound of formula A_2B_3 has the hcp lattice. Which atom forms the hcp lattice and what fraction of tetrahedral voids is occupied by the other atoms? **[2019, 10 Jan Shift-II]**

(a) hcp lattice- A, $\frac{2}{3}$ tetrahedral voids-B

(b) hcp lattice-A, $\frac{1}{3}$ tetrahedral voids-B

(c) hcp lattice-B, $\frac{1}{3}$ tetrahedral voids-A

(d) hcp lattice-B, $\frac{2}{3}$ tetrahedral voids-A

Ans. ***(c)***

Total effective number of atoms in hcp unit lattice

= Number of octahedral voids in hcp = 6

∴ Number of tetrahedral voids (TV) in hcp

= 2 × Number of atoms in hcp lattice

= 2 × 6 = 12

As, formula of the lattice is A_2B_3.

Suppose,	A	B
	$\left(\frac{1}{3}\times TV\right)$	(hcp)
⇒	$\frac{1}{3}\times 12$	6
⇒	$\frac{2}{3}$	1
⇒	2	3

So, $A = \frac{1}{3}$ tetrahedral voids,

B = hcp lattice

65 A solid having density of $9\times10^3\,kg\,m^{-3}$ forms face centred cubic crystals of edge length $200\sqrt{2}$ pm. What is the molar mass of the solid? [Avogadro constant $= 6\times10^{23}\,mol^{-1}, \pi = 3$] **[2019, 11 Jan Shift-I]**

(a) $0.03050\,kg\,mol^{-1}$

(b) $0.4320\,kg\,mol^{-1}$

(c) $0.0432\,kg\,mol^{-1}$

(d) $0.0216\,kg\,mol^{-1}$

Ans. ***(a)***

Density of a crystal

$$d = \frac{M\times Z}{N_A\times a^3} \Rightarrow M = \frac{d\times N_A\times a^3}{Z}$$

Given, $d = 9\times10^3\,kg\,m^{-3}$

M = Molar mass of the solid

$Z = 4$ (for fcc crystal)

N_A = Avogadro's constant $= 6\times10^{23}\,mol^{-1}$

a = Edge length of the unit cell $= 200\sqrt{2}\,pm = 200\sqrt{2}\times10^{-12}\,m$

On substituting all the given values, we get

$$= \frac{(9\times10^3)\,kg\,m^{-3}\times(6\times10^{23})\,mol^{-1}\times(200\sqrt{2}\times10^{-12})^3\,m^3}{4}$$

$$= 0.0305\,kg\,mol^{-1}$$

66 The radius of the largest sphere which fits properly at the centre of the edge of a body centred cubic unit cell is
(Edge length is represented by 'a') **[2019, 11 Jan Shift-II]**

(a) 0.134 a (b) 0.027 a

(c) 0.047 a (d) 0.067 a

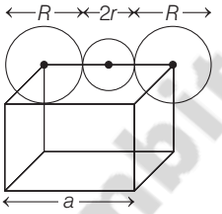
Ans. ***(d)***

For body centred cubic bcc structure,

$$\text{radius}\,(R) = \frac{\sqrt{3}}{4}a \quad ...(i)$$

Where, a = edge length

According to question, the structure of cubic unit cell can be shown as follows:



$$\therefore \quad a = 2(R + r) \quad ...(ii)$$

On substituting the value of R from Eq. (i) to Eq. (ii), we get

$$\frac{a}{2} = \frac{\sqrt{3}}{4}a + r$$

$$\Rightarrow \quad r = \frac{a}{2} - \frac{\sqrt{3}}{4}a = \frac{2a - \sqrt{3}a}{4}$$

$$r = \frac{a(2-\sqrt{3})}{4}$$

$$\Rightarrow \quad r = 0.067a$$

67 A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be **[JEE Main 2017]**

(a) $2a$ (b) $2\sqrt{2}\,a$

(c) $\sqrt{2}\,a$ (d) $\frac{a}{\sqrt{2}}$

Ans. ***(d)***

For fcc arrangement, $4r = \sqrt{2}a$

where, r = radius and a = edge length

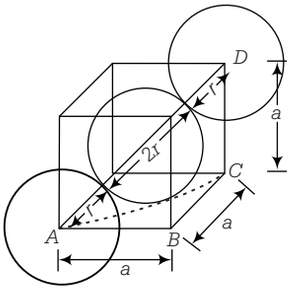
$$\therefore \text{Closest distance} = 2r = \frac{\sqrt{2}\,a}{2} = \frac{a}{\sqrt{2}}$$

68 Sodium metal crystallises in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately **[JEE Main 2015]**

(a) 1.86 Å (b) 3.22 Å

(c) 5.72 Å (d) 0.93 Å

Ans. ***(a)***



From this figure,

$$(AC)^2 = (AB)^2 + (BC)^2$$

$$\Rightarrow \quad (AC)^2 = a^2 + a^2 = 2a^2$$

Also, $(AD)^2 = (AC)^2 + (DC)^2$

$$\Rightarrow \quad (4r)^2 = 2a^2 + a^2$$

$$16r^2 = 3a^2$$

$$\Rightarrow \quad r = \frac{\sqrt{3}}{4}a$$

Now, when Na metal crystallises in bcc unit cell with unit cell edge, a = 4.29 Å

We have the formula for radius,

i.e. $r = \frac{\sqrt{3}}{4}\times 4.29\,Å = 1.86\,Å$

69 CsCl crystallises in body centered cubic lattice. If 'a' its edge length, then which of the following expressions is correct?

(a) $r_{Cs^+} + r_{Cl^-} = 3a$ **[JEE Main 2014]**

(b) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$

(c) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$

(d) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$

Ans. ***(c)***

In CsCl, Cl^- lie at the corners of simple cube and Cs^+ at the body centre. Therefore, along the body diagonal, Cs^+ and Cl^- touch each other.

Hence, $\frac{\sqrt{3}}{2}a = r_{Cs^+} + r_{Cl^-}$

70 Which of the following exists as covalent crystals in the solid state? **[JEE Main 2013]**

(a) Iodine (b) Silicon

(c) Sulphur (d) Phosphorus

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Ans. ***(b)***

Silicon exists as covalent crystal in solid state.
(Network like structure, like diamond).

71 Lithium forms body-centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be **[AIEEE 2012]**

(a) 75 pm (b) 300 pm
(c) 240 pm (d) 152 pm

Ans. ***(d)***

In body-centred cubic structure,
Edge length = a = 351 pm, Radius = r = ?

Then, $r = \frac{\sqrt{3}a}{4}$

$= \frac{\sqrt{3} \times 351}{4} = 152$ pm

72 In a face-centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centred positions. If one atom of B is missing from one of the face centred points, the formula of the compound is **[AIEEE 2011]**

(a) A_2B (b) AB_2
(c) A_2B_2 (d) A_2B_2

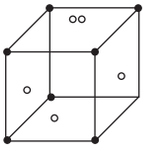
Ans. ***(d)***

Number of atoms (A) per unit cell

$= 8 \times \frac{1}{8} = 1$

Number of atoms (B) per unit cell

$= (6 - 1) \times \frac{1}{2} = \frac{5}{2}$ (one atom B is missing)



Thus, formula is $A_1B_{5/2} = A_2B_5$

73 Copper crystallises in fcc lattice with a unit cell edge of 361 pm. The radius of copper atom is **[AIEEE 2011]**

(a) 181 pm (b) 108 pm
(c) 128 pm (d) 157 pm

Ans. ***(c)***

Copper crystallises in fcc lattice.
If, r = radius, a = edge length

then $r = \frac{a}{2\sqrt{2}} = \frac{361}{2\sqrt{2}}$ pm

$= 127.633$ pm ≈ 128 pm

74 The edge length of a face centered cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is **[AIEEE 2010]**

(a) 288 pm (b) 398 pm
(c) 618 pm (d) 144 pm

Ans. ***(d)***

For fcc arrangement

$2(r^+ + r^-)$ = edge length

$2(110 + r^-) = 508$

So, $r^- = 144$ pm

75 Percentage of free space in cubic close packed structure and in body centred packed structure are respectively **[AIEEE 2010]**

(a) 30% and 26% (b) 26% and 32%
(c) 32% and 48% (d) 48% and 26%

Ans. ***(b)***

Packing fraction of ccp $= \frac{\pi}{3\sqrt{2}} = 0.74$

$\Rightarrow 74\%$

% free space in ccp = 26%

Packing fraction of bcc $= \frac{\pi\sqrt{3}}{8} = 0.68$

$= 68\%$ % free space in bcc = 32%

76 Copper crystallises in fcc with a unit cell length of 361 pm. What is the radius of copper atom? **[AIEEE 2009]**

(a) 108 pm (b) 127 pm
(c) 157 pm (d) 181 pm

Ans. ***(b)***

In fcc unit cell $\sqrt{2}a = 4r$

$r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 361}{4} = 127$ pm

77 In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be **[AIEEE 2008]**

(a) X_4Y_3 (b) X_2Y_3
(c) X_2Y (d) X_3Y_4

Ans. ***(a)***

Suppose atoms of element Y in ccp = 100
Number of tetrahedral voids = 2×100
Number of atoms of element

$X = \frac{2}{3} \times 200 = \frac{400}{3}$

$\Rightarrow \frac{X}{Y} = \frac{400}{300}$

Formula = X_4Y_3

78 Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius) **[AIEEE 2006]**

(a) $\frac{20}{3}\pi r^3$ (b) $\frac{24}{3}\pi r^3$
(c) $\frac{12}{3}\pi r^3$ (d) $\frac{16}{3}\pi r^3$

Ans. ***(d)***

Total number of atoms in face centred cubic unit cell = 4

At corner $= 8 \times \frac{1}{8} = 1$

On faces $= 6 \times \frac{1}{2} = 3$

Total = 4

Total volume $= 4 \times \frac{4\pi r^3}{3} = \frac{16}{3}\pi r^3$

79 An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula for this compound would be **[AIEEE 2005]**

(a) A_3B (b) AB_3
(c) A_2B (d) AB

Ans. ***(b)***

Unit cell consists of A ions at the corners.

Thus, number of ions of the type

$A = \frac{8}{8} = 1$

Unit cell consists of B ions at the centre of the six faces.

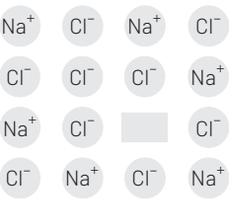
Thus, number of ions of the type

$B = \frac{6}{2} = 3$

[Each corner is shared by 8 cubes and each face is shared by 2 faces]

Thus, formula is AB_3.

80 What type of crystal defect is indicated in the diagram shown below? **[AIEEE 2004]**



(a) Frenkel defect
(b) Schottky defect
(c) Interstitial defect
(d) Frenkel and Schottky defects

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Ans. ***(b)***

When equal number of cations and anions (such that charges are equal) are missing ($1Na^+$, $1Cl^-$ / $1Fe^{2+}$, $2Cl^-$) then, it is a case of Schottky defect.

81 How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g?
[Atomic mass : Na = 23, Cl = 35.5]
[AIEEE 2003]

(a) 2.57×10^{21} (b) 5.14×10^{21}
(c) 1.28×10^{21} (d) 1.71×10^{21}

Ans. ***(a)***

Mass of one unit cell
(m) = volume × density

$$= a^3 \times d$$

$$= a^3 \times \frac{MZ}{N_0 a^3} = \frac{MZ}{N_0}$$

$$m = \frac{58.5\times4}{6.02\times10^{23}}\text{g}$$

$$\therefore \text{Number of unit cells in 1g} = \frac{1}{m}$$

$$= \frac{6.02\times10^{23}}{58.5\times4}$$

$$= 2.57\times10^{21}$$

82 Number of atoms in the unit cell of Na (bcc type crystal) and Mg (fcc type crystal) are, respectively
[AIEEE 2002]

(a) 4, 4 (b) 4, 2
(c) 2, 4 (d) 1, 1

Ans. ***(c)***

In Na unit cell (body centred cubic)

$$8\,(\text{corner atoms})\times\frac{1}{8}=1$$

Atoms placed inside the unit cell = 1

Total atoms = 2

In Mg unit cell (face centred cubic)

$$8\,(\text{corner atoms})\times\frac{1}{8}=1$$

$$6\,(\text{face atoms})\times\frac{1}{2}=3$$

Total atoms = 4

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03

Atomic Structure

TOPIC 1
Preliminary Models

01 If the Thomson model of the atom was correct, then the result of Rutherford's gold foil experiment would have been

(a) all of the α-particles pass through the gold foil without decrease in speed.
(b) α-particles are deflected over a wide range of angles.
(c) all α-particles get bounced back by 180°.
(d) α-particles pass through the gold foil deflected by small angles and with reduced speed.

[2021, 27 July Shift-II]

Ans. ***(d)***

According to Thomson model of atom, positive charge and mass of atom is uniformely distributed and electrons are embedded in it like seeds in water melon.

Hence, if we strike α-particles (consisting of 2 positive charge protons and 2 neutral neutrons i.e. of heavier mass than 1 proton) on a thin gold foil then α-particles will pass through the gold foil and will deflected by some angle (due to charge repulsion) with reduced speed.

This result is depicted in option (d) that α-particles pass through the gold foil deflected by small angle with reduced speed.

02 Hydrogen has three isotopes (*A*), (*B*) and (*C*). If the number of neutron(s) in (*A*), (*B*) and (*C*) respectively, are (*x*), (*y*) and (*z*), the sum of (*x*), (*y*) and (*z*) is **[2020, 8 Jan Shift-II]**

(a) 4 (b) 3
(c) 2 (d) 1

Ans. ***(b)***

Number of neutrons in protium (^1_1H) is zero (*x*).

Number of neutrons in deuterium (^2_1H or ^2_1D) is 1 (*y*)

Number of neutrons in tritium (^3_1H or ^3_1T) is 2 (*z*)

So, the sum of *x* , *y* and *z* is $x + y + z = 3$

TOPIC 2
Bohr's Model and Hydrogen Spectrum

03 The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is equal to $\frac{h^2}{xma_0^2}$.

The value of 10*x* is ..... .
(a_0 is radius of Bohr's orbit)
(Nearest integer) [Given, $\pi = 3.14$]

[2021, 27 Aug Shift-I]

Ans. ***(3155)***

$\because$ Angular moment is given as,

$$mvr = \frac{nh}{2\pi}$$

$$\therefore \text{Kinetic energy} = \frac{n^2h^2}{8\pi^2mr^2} = \frac{4h^2}{8\pi^2m(4a_0)^2}$$

$$= \left(\frac{4}{8\pi^2 \times 16}\right)\frac{h^2}{ma_0^2} = \frac{h^2}{xma_0^2} \quad \text{(Given)}$$

$$x = \frac{4}{8\pi^2 \times 16}$$

$$\Rightarrow \quad x = 315.507$$

$$10x = 3155.07$$

04 Given below are two statements.

Statement I According to Bohr's model of an atom, qualitatively the magnitude of velocity of electron increases with decrease in positive charges on the nucleus as there is no strong hold on the electron by the nucleus.

Statement II According to Bohr's model of an atom, qualitatively the magnitude of velocity of electron increases with decrease in principal quantum number.

In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 26 Aug Shift-I]

(a) Both statement I and statement II are false.
(b) Both statement I and statement II are true.
(c) Statement I is false but statement II is true.
(d) Statement I is true but statement II is false.

Ans. ***(c)***

According to Bohr's atom, velocity of electron is given by,

$$v \propto \frac{Z}{n} \qquad \ldots(i)$$

where, *v* = velocity of electron

Z = atomic number of atom

n = principal quantum number

From Eq. (i), velocity of electron is directly proportional to atomic number of atom, corresponding to positive charge. So, as *Z* increases velocity also increases. Hence, statement I is false.

Also, velocity of electron is inversely proportional to *n* i.e. as '*n*' decreases velocity of electron increases. So, statement II is true.

05 Given below are two statements.

Statement I Bohr's theory accounts for the stability and line spectrum of Li^+ ion.

Statement II Bohr's theory was unable to explain the splitting of spectral lines in the presence of a magnetic field.

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In the light of the above statements, choose the most appropriate answer from the options given below :
[2021, 18 March Shift-II]

(a) Both statements I and II are true.
(b) Statement I is false but statement II is true.
(c) Both statements I and II are false.
(d) Statement I is true but statement II is false.

Ans. ***(b)***

Statement I is false, because Bohr's theory accounts for the stability and spectrum of single electronic species (e.g. He^+, Li^{2+} etc.) but Li^+ has two electrons.

Bohr's theory fails to explain splitting of spectral lines in presence of magnetic field i.e. Zeeman effect .

$\therefore$ Statement II is true.

06 Electromagnetic radiation of wavelength 663 nm is just sufficient to ionise the atom of metal *A*. The ionisation energy of metal *A* in kJ mol^{-1} is ..... . (Rounded off to the nearest integer)

[$h = 6.63 \times 10^{-34}$ J-s, $c = 3.00 \times 10^8$ ms^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}]
[2021, 25 Feb Shift-II]

Ans. ***(180)***

Energy of EMR = IE of the metal (*A*)

$$= h\nu = \frac{hc}{\lambda}\ \text{atom}^{-1} = -\frac{hc}{\lambda} \times N_A\ \text{mol}^{-1}$$

$$= \frac{(6.63 \times 10^{-34}) \times (3 \times 10^8) \times (6.02 \times 10^{23})}{(663 \times 10^{-9})}\ \text{J mol}^{-1}$$

$[\because \lambda = 663\ \text{nm} = 663 \times 10^{-9}\ \text{m}]$

$= 180600\ \text{J mol}^{-1} = 180.6\ \text{kJ mol}^{-1}$

$\simeq 180\ \text{kJ mol}^{-1}$

07 According to Bohr's atomic theory,

I. kinetic energy of electron is $\propto \frac{Z^2}{n^2}$
II. the product of velocity (*v*) of electron and principal quantum number (*n*), '*vn*' $\propto Z^2$.
III. frequency of revolution of electron in an orbit is $\propto \frac{Z^3}{n^3}$
IV. coulombic force of attraction on the electron is $\propto \frac{Z^3}{n^4}$

Choose the most appropriate answer from the options given below. **[2021, 24 Feb Shift-II]**

(a) Only III (b) Only I
(c) I, III and IV (d) I and IV

Ans. ***(d)***

According to Bohr's theory,

I. $KE \propto \frac{Z^2}{n^2}$ or $13.6 \propto \frac{Z^2}{n^2}\frac{(eV)}{(atom)}$, ($\therefore$ Correct)

II. Speed of electron $\propto \frac{Z}{n}$

(Here, Z = atomic number, n = number of shells)

$\therefore \quad v \times n \propto Z$ ($\therefore$ Incorrect)

III. Frequency of revolution of electron $= \frac{v}{2\pi r}$

Frequency $\propto \frac{Z^2}{n^3}$ $\left(\because v \propto \frac{z}{n},\ r \propto \frac{n^2}{z}\right)$

($\therefore$ Incorrect)

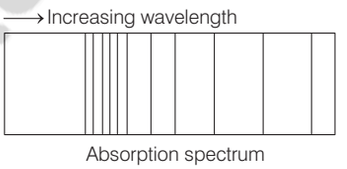
IV. $F = \frac{kq_1q_2}{r^2} = \frac{kZe^2}{r^2}$

$$F = \frac{Z}{\left(\frac{n^2}{Z}\right)^2}$$

$F \propto \frac{Z^3}{n^4}$ ($\therefore$ Correct)

Hence, only I, and IV are correct.

08 The figure that is not a direct manifestation of the quantum nature of atoms is
[2020, 2 Sep Shift-I]

(a)


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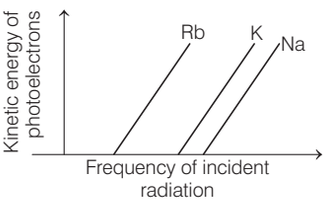
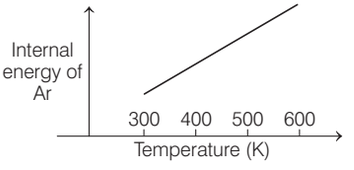
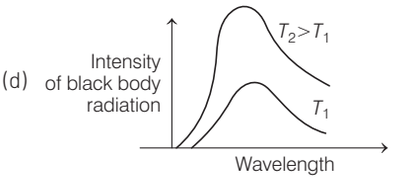


(c)


(d)


Ans. ***(c)***

Quantum nature of atoms are associated with following phenomena or processes

(i) Absorption spectrum
(ii) Emission spectrum
(iii) Black body radiation
(iv) Photo-electricity

Internal energy (U) of particles like atoms depends upon the thermodynamic variables (p, V, T) of the system. Thus, $U = f(p,T)$

or $U = f_1(T, V)$

or $U = f_2(p, V)$

So, quantum nature of atom is not associated with its internal energy.

Graph (c) is not a direct manifestation of the quantum nature of atoms.

09 The region in the electromagnetic spectrum where the Balmer series lines appear is **[2020, 4 Sep Shift-I]**

(a) infrared (b) ultraviolet
(c) microwave (d) visible

Ans. ***(d)***

Balmer series lies in the visible region of the electromagnetic spectrum. Photons that correspond to these energies will not strongly absorb highly excited hydrogen gas. So, there is the possibility for detecting absorption at Balmer line wave length.

Paschen, Brackett and Pfund series lies in the infrared region whereas, only Layman series lies in the ultraviolet region of the electromagnetic spectrum.

10 The shortest wavelength of H atom in the Lyman series is λ_1. The longest wavelength in the Balmer series of He^+ is **[2020, 4 Sep Shift-II]**

(a) $\frac{36\lambda_1}{5}$ (b) $\frac{5\lambda_1}{9}$ (c) $\frac{9\lambda_1}{5}$ (d) $\frac{27\lambda_1}{5}$

Ans. ***(c)***

As we know that $\Delta E = \frac{hc}{\lambda}$

Hence, λ will be, $\lambda = \frac{hc}{\Delta E}$

For, λ = minimum, i.e. shortest, ΔE = maximum

For Lyman series, $n = 1$ and for ΔE_{max} transition must be form $n = \infty$ to $n = 1$.

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So, $\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ ($\because n_1 = 1$ and $n_2 = \infty$)

$$\frac{1}{\lambda} = R_H\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) \times (1)^2$$

$$\frac{1}{\lambda} = R_H (1-0)$$

$$\Rightarrow \frac{1}{\lambda} = R \times (1)^2$$

$$\Rightarrow \lambda_1 = \frac{1}{R}$$

For longest wavelength, ΔE = minimum for Balmer series, $n = 3$ to $n = 2$ will have ΔE minimum.

For He^+, $Z = 2$

So, $\frac{1}{\lambda_2} = R_H \times 2^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$$\frac{1}{\lambda_2} = R_H \times 4\left(\frac{1}{4} - \frac{1}{9}\right), \frac{1}{\lambda_2} = R_H \times 4 \times \frac{5}{36}$$

$$\frac{1}{\lambda_2} = R_H \times \frac{5}{9}$$

$$\Rightarrow \lambda_2 = \lambda_1 \times \frac{9}{5}$$

11 The difference between the radii of 3rd and 4th orbits of Li^{2+} is ΔR_1. The difference between the radii of 3rd and 4th orbits of He^+ is ΔR_2. Ratio $\Delta R_1 : \Delta R_2$ is **[2020, 5 Sep Shift-I]**

(a) 3 : 2 (b) 8 : 3
(c) 2 : 3 (d) 3 : 8

Ans. ***(c)***

We know that $r = 0.529 \frac{n^2}{Z}$ Å

For Li^{2+} $(r_{Li^{2+}})_{n=4} - (r_{Li^{2+}})_{n=3}$

$$\Rightarrow \frac{0.529}{3}(16-9) = \Delta R_1 \quad ...(i)$$

For He^+ $(r_{He^+})_{n=4} - (r_{He^+})_{n=3}$

$$\Rightarrow \frac{0.529}{3}(16-9) = \Delta R_2 \quad ...(ii)$$

$$\frac{\Delta R_1}{\Delta R_2} = \frac{\frac{0.529}{3}(16-9)}{\frac{0.529}{2}(16-9)} = \frac{2}{3}$$

Hence, the ratio of $\Delta R_1 : \Delta R_2$ is 2 : 3.

12 For the Balmer series in the spectrum of H atom, $\bar{\nu} = R_H \left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\}$, the correct statements among (I) to (IV) are :

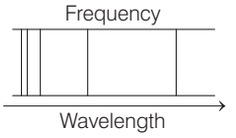
(I) As wavelength decreases, the lines in the series converge
(II) The integer n_1 is equal to 2
(III) The lines of longest wavelength corresponds to $n_2 = 3$
(IV) The ionisation energy of hydrogen can be calculated from wave number of these lines **[2020, 8 Jan Shift-I]**

(a) I, II, IV (b) II, III, IV
(c) I, III, IV (d) I, II, III

Ans. ***(d)***

Statements I, II and III are correct. The explanations of these statements are as follows :

(I) In each series of hydrogen spectrum, lines converge at the higher frequency or lower wavelength limit.



∴ This is correct.

(II) For Balmer series, $n_1 = 2$

∴ This is correct.

(III) Longest wavelength represents the smallest wave number

$$\bar{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). (n_2 > n_1)$$

When $n_1 = 2$, smallest value of $\bar{\nu}$ is for $n_2 = 3$

∴ This is a correct statement.

(IV) This statement is not correct. It's corrected form is as follows: Ionisation energy of hydrogen can be calculated from Lyman series lines ($n = 1$) only by using the following formula,

$$\bar{\nu} = R_H\left[\frac{1}{(1)^2} - \frac{1}{\infty^2}\right]$$

13 The radius of the second Bohr orbit in terms of the Bohr radius, a_0, in Li^{2+} is **[2020, 8 Jan Shift-II]**

(a) $\frac{2a_0}{3}$ (b) $\frac{4a_0}{3}$ (c) $\frac{4a_0}{9}$ (d) $\frac{2a_0}{9}$

Ans. ***(b)***

According to Bohr model, radius of orbit $r_n = \frac{a_0 \times n^2}{Z}$, where a_0 = Bohr radius (Radius of 1st orbit of H-atom)

For, Li^{2+}, $Z = 3$ and $n = 2$

$$\therefore r = \frac{2^2 \times a_0}{3} = \frac{4a_0}{3}$$

14 For any given series of spectral lines of atomic hydrogen, let $\Delta\bar{\nu} = \bar{\nu}_{max} - \bar{\nu}_{min}$ be the difference in maximum and minimum frequencies in cm^{-1}. The ratio $\Delta\bar{\nu}_{Lyman} / \Delta\bar{\nu}_{Balmer}$ is **[2019, 9 April Shift-I]**

(a) 27 : 5 (b) 5 : 4 (c) 9 : 4 (d) 4 : 1

Ans. ***(c)***

For any given series of spectral lines of atomic hydrogen.

Let $\Delta\bar{\nu} = \bar{\nu}_{max} - \bar{\nu}_{min}$ be the difference in maximum and minimum frequencies in cm^{-1}.

For Lyman series,

$$\Delta\bar{\nu} = \bar{\nu}_{max} - \bar{\nu}_{min}$$

General formula: $\bar{\nu} = 109677\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$

For Lyman $n_1 = 1$, $n_2 = 2, 3, \ldots$

$$\bar{\nu}_{max} = 109{,}677\left(\frac{1}{1} - \frac{1}{\infty}\right) = 109{,}677\left(\frac{1}{1} - 0\right)$$

$$= 109{,}677$$

$$\bar{\nu}_{min} = 109{,}677\left(\frac{1}{1} - \frac{1}{(2)^2}\right)$$

$$\Delta\bar{\nu}_{Lyman} = \bar{\nu}_{max} - \bar{\nu}_{min}$$

$$= 109{,}677 - \left[\frac{109{,}677 \times 3}{4}\right] = \frac{109{,}677}{4}$$

For Balmer series,

$$\bar{\nu}_{max} = 109{,}677\left(\frac{1}{(2)^2} - \frac{1}{\infty}\right) \Rightarrow \frac{109677}{4}$$

$$\bar{\nu}_{min} = 109{,}677\left(\frac{1}{(2)^2} - \frac{1}{(3)^2}\right)$$

$$\Rightarrow \frac{109677 \times 5}{36}$$

$$\Delta\bar{\nu} = \bar{\nu}_{max} - \bar{\nu}_{min}$$

$$\Delta\bar{\nu}_{Balmer} = \frac{109{,}677}{4} - \left[\frac{109{,}677}{36} \times 5\right]$$

$$= 109{,}677\left(\frac{1}{9}\right)$$

$$\frac{\Delta\bar{\nu}_{Lyman}}{\Delta\bar{\nu}_{Balmer}} = \frac{109{,}677/4}{109{,}677/9}$$

$$\Rightarrow \frac{\Delta\bar{\nu}_{Lyman}}{\Delta\bar{\nu}_{Balmer}} = \frac{9}{4}$$

∴ The ratio of $\frac{\Delta\bar{\nu}_{Lyman}}{\Delta\bar{\nu}_{Balmer}}$ is 9 : 4.

15 The ratio of the shortest wavelength of two spectral series of hydrogen spectrum is found to be about 9. The spectral series are **[2019, 10 April Shift-II]**

(a) Lyman and Paschen
(b) Brackett and Pfund
(c) Paschen and Pfund
(d) Balmer and Brackett

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Ans. ***(a)***

According to Rydberg's equation,

$$\frac{1}{\lambda} = \frac{R_H}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or $$\frac{1}{\lambda} \propto \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For shortest wavelength, i.e. highest energy spectral line, n_2 will be (∞).

For the given spectral series, ratio of the shortest wavelength of two spectral series can be calculated as follows :

(a) $\frac{\lambda_L}{\lambda_P} = \frac{\frac{1}{3^2} - \frac{1}{\infty^2}}{\frac{1}{1^2} - \frac{1}{\infty^2}} = \frac{\frac{1}{9} - 0}{1 - 0} = \frac{1}{9}$

(b) $\frac{\lambda_{Bk}}{\lambda_{Pf}} = \frac{\frac{1}{5^2} - \frac{1}{\infty^2}}{\frac{1}{4^2} - \frac{1}{\infty^2}} = \frac{1}{25} \times \frac{16}{1} = \frac{16}{25}$

(c) $\frac{\lambda_P}{\lambda_{Pf}} = \frac{\frac{1}{5^2} - \frac{1}{\infty^2}}{\frac{1}{3^2} - \frac{1}{\infty^2}} = \frac{1}{25} \times \frac{9}{1} = \frac{9}{25}$

(d) $\frac{\lambda_B}{\lambda_{Bk}} = \frac{\frac{1}{4^2} - \frac{1}{\infty^2}}{\frac{1}{2^2} - \frac{1}{\infty^2}} = \frac{1}{16} \times \frac{4}{1} = \frac{1}{4}$

Note Lyman = L ($n_1 = 1$), Balmer = B ($n_1 = 2$)

Paschen = P ($n_1 = 3$), Brackett = Bk ($n_1 = 4$)

Pfund = Pf ($n_1 = 5$)

16 For emission line of atomic hydrogen from $n_i = 8$ to $n_f = n$, the plot of wave number (ν) against $\left(\frac{1}{n^2}\right)$ will be (The Rydberg constant, R_H is in wave number unit)

(a) non linear

(b) linear with slope $-R_H$

(c) linear with slope R_H

(d) linear with intercept $-R_H$

[2019, 9 Jan Shift-I]

Ans. ***(c)***

According to Rydberg's formula,

wave number $(\bar{\nu}) = R_H Z^2\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$

Given, $n_i = n,\ n_f = 8$

[$\because$ it is the case of emission]

$$\bar{\nu} = R_H \times (1)^2\left[\frac{1}{n^2} - \frac{1}{8^2}\right]$$

$$\bar{\nu} = R_H\left[\frac{1}{n^2} - \frac{1}{64}\right] = \frac{R_H}{n^2} - \frac{R_H}{64}$$

On comparing with equation of straight line, $y = mx + c$, we get

Slope $= R_H$, intercept $= \frac{-R_H}{64}$.

Thus, plot of wave number $(\bar{\nu})$ against $\frac{1}{n^2}$ will be linear with slope $(+R_H)$.

17 The ground state energy of hydrogen atom is –13.6 eV. The energy of second excited state of He^+ ion in eV is **[2019, 10 Jan Shift-II]**

(a) -54.4 (b) - 3.4 (c) - 6.04 (d) - 27.2

Ans. ***(c)***

The ground state energy of H-atom is + 13.6 eV.

For second excited state, $n = 2 + 1 = 3$

$$\therefore\ E_3(He^+) = -13.6 \times \frac{Z^2}{n^2}\ \text{eV} \quad [\because \text{for } He^+,\ Z = 2]$$

$$= -13.6 \times \frac{2^2}{3^2}\ \text{eV} = -6.04\ \text{eV}$$

18 Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose? [$R_H = 1 \times 10^5\ cm^{-1}$, $h = 6.6 \times 10^{-34}$ Js, $c = 3 \times 10^8\ ms^{-1}$]

(a) Paschen, $5 \to 3$ (b) Paschen, $\infty \to 3$

(c) Lyman, $\infty \to 1$ (d) Balmer, $\infty \to 2$

[2019, 11 Jan Shift-I]

Ans. ***(b)***

$$\Delta E = hc \times \frac{1}{\lambda} = hc \times \left[R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \times Z^2\right]$$

$$\Rightarrow \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{hc}{R_H \times \lambda \times Z^2 \times hc} \quad [\text{for H, atom } Z = 1]$$

$$= \frac{1}{R_H \times \lambda} = \frac{1}{(1 \times 10^7\ m^{-1})} \times \frac{1}{(900 \times 10^{-9}\ m)}$$

$$\Rightarrow \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{1}{9}$$

So, in option (b) $\frac{1}{3^2} - \frac{1}{\infty^2} = \frac{1}{9} - 0 = \frac{1}{9}$ $\left[\because n_1 = 3,\ n_2 = \infty\right]$

19 The radius of the second Bohr orbit for hydrogen atom is (Planck's constant (h) $= 6.6262 \times 10^{-34}$ Js; mass of electron $= 9.1091 \times 10^{-31}$ kg ; charge of electron (e) $= 1.60210 \times 10^{-19}$ C; permitivity of vacuum (ϵ_0) $= 8.854185 \times 10^{-12}$ $kg^{-1}m^{-3}A^2$) **[JEE Main 2017]**

(a) 1.65 Å (b) 4.76 Å

(c) 0.529 Å (d) 2.12 Å

Ans. ***(d)***

Bohr radius $(r_n) = \epsilon_0\ n^2h^2$

$$r_n = \frac{n^2h^2}{4\pi^2 me^2 kZ} \Rightarrow k = \frac{1}{4\pi\epsilon_0}$$

$$\therefore\quad r_n = \frac{n^2h^2\epsilon_0}{\pi me^2 Z} = n^2\frac{a_0}{Z}$$

where, m = mass of electron, e = charge of electron

h = Planck's constant,

k = Coulomb constant

$$r_n = \frac{n^2 \times 0.53}{Z}\ \text{Å}$$

Radius of n^{th} Bohr orbit for H-atom $= 0.53\ n^2$ Å [$Z = 1$ for H-atom]

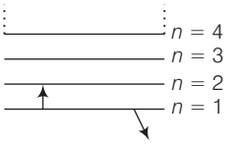
$\therefore$ Radius of 2^{nd} Bohr orbit for H-atom $= 0.53 \times (2)^2 = 2.12$ Å

20 Which of the following is the energy of a possible excited state of hydrogen? **[JEE Main 2015]**

(a) + 13.6 eV (b) – 6.8 eV

(c) – 3.4 eV (d) + 6.8 eV

Ans. ***(c)***



Maximum population of e^- of H-atom

Since, at $n = 1$, the population of electrons is maximum *i.e.* at ground state. So, maximum excitation will take place from $n = 1$ to $n = 2$.

Hence, $n = 2$ is the possible excited state.

Now, we have the formula for energy of H-atom

$$(E_n)_H = -13.6\frac{Z^2}{n^2}\ \text{eV}$$

where, Z = atomic number

Z for H-atom = 1

$$\therefore\quad (E_n)_H = -13.6 \times \frac{1}{2^2}\text{eV}$$

$$= -\frac{13.6}{4}\text{eV} = -3.4\ \text{eV}$$

21 Energy of an electron is given by $E = -2.178 \times 10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right)$.

Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be ($h = 6.62 \times 10^{-34}$ J s and $c = 3.0 \times 10^8\ ms^{-1}$) **[JEE Main 2013]**

(a) 1.214×10^{-7} m (b) 2.816×10^{-7} m

(c) 6.500×10^{-7} m (d) 8.500×10^{-7} m

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Ans. ***(a)***

Energy change

$$\Delta E = 2.178\times10^{-18}\left(\frac{1}{1^2}-\frac{1}{2^2}\right)=\frac{hc}{\lambda}$$

$$=2.178\times10^{-18}\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

$$=\frac{6.62\times10^{-34}\times3.0\times10^{8}}{\lambda}$$

$$\Rightarrow \lambda \approx 1.214\times10^{-7}\ \text{m}$$

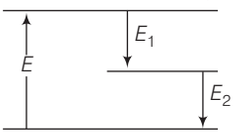
22 A gas absorbs photon of 355 nm and emits at two wavelengths. If one of the emission is at 680 nm, the other is at **[AIEEE 2011]**

(a) 1035 nm (b) 325 nm
(c) 743 nm (d) 518 nm

Ans. ***(c)***

Energy values are always additive.

$$E_{total} = E_1 + E_2 \Rightarrow \frac{hc}{\lambda}=\frac{hc}{\lambda_1}+\frac{hc}{\lambda_2}$$



$$\therefore \quad \frac{1}{\lambda}=\frac{1}{\lambda_1}+\frac{1}{\lambda_2}$$

$$\Rightarrow \quad \frac{1}{355}=\frac{1}{680}+\frac{1}{\lambda_2}$$

$$\lambda_2 = 742.77\ \text{nm}$$

$$\approx 743\ \text{nm}$$

23 The frequency of light emitted for the transition $n=4$ to $n=2$ of He^+ is equal to the transition in H atom corresponding to which of the following? **[AIEEE 2011]**

(a) $n=3$ to $n=1$ (b) $n=2$ to $n=1$
(c) $n=3$ to $n=2$ (d) $n=4$ to $n=3$

Ans. ***(b)***

$$\Delta E = hu = \frac{2\pi^2 mZ^2e^4k^2}{h^2}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

if electron falls from n_2-level to n_1- level.

$\therefore$ In He^+, for $n_2=4$ to $n_1=2$ transition

$$\nu_{He^+} = \text{constant}\,(4)\left[\frac{1}{2^2}-\frac{1}{4^2}\right] \quad [\because Z_{He^+}=2]$$

$$=\text{constant}\times4\left[\frac{3}{16}\right]$$

$$=\frac{3}{4}\times\text{constant}$$

$$\nu(\text{H}) = \text{constant}\,(1)^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$=\text{constant}\times\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

(a) For $n_2=3$ and $n_1=1$,

$$\nu(\text{H}) = \text{constant}\left[\frac{1}{1}-\frac{1}{9}\right]$$

$$=\frac{8}{9}\times\text{constant}\neq\frac{3}{4}\times\text{constant}$$

(b) For $n_2=2$ and $n_1=1$,

$$\nu(\text{H}) = \text{constant}\times\left[\frac{1}{1}-\frac{1}{4}\right]$$

$$=\frac{3}{4}\times\text{constant}\ =\nu(\text{He}^+)$$

(c) For $n=3$ and $n_1=2$

$$\nu(\text{H}) = \text{constant}\times\left[\frac{1}{2^2}-\frac{1}{3^2}\right]$$

$$=\frac{5}{36}\times\text{constant}\neq\nu(\text{He}^+)$$

(d) For $n_2=4$ and $n_1=3$

$$\nu(\text{H}) = \text{constant}\times\left[\frac{1}{3^2}-\frac{1}{4^2}\right]$$

TOPIC 3
Wave Particle and Quality of Matter

24 A 50 watt bulb emits monochromatic red light of wavelength of 795 nm. The number of photons emitted per second by the bulb is $x\times10^{20}$. The value of x is ..... .

[Given, $h=6.63\times10^{-34}$ Js and $c=3.0\times10^{8}\ \text{ms}^{-1}$]

[2021, 1 Sep Shift-II]

Ans. ***(2)***

Energy of photon is given as

$$E=\frac{nhc}{\lambda} \qquad ...(i)$$

where, E = energy of photon (50 W),
n = number of photon
h = Planck's constant (6.63×10^{-34} J s)
c = speed of light (3×10^{8} m / s)
λ = wavelength of light (795×10^{-9} m)
E = 50 W = 50 J = energy of photon

$$50\ \text{J}=\frac{n\times6.63\times10^{-34}\ \text{J s}\times3\times10^{8}\ \text{m/s}}{795\times10^{-9}\ \text{m}}$$

$$\Rightarrow \quad n=\frac{50\times795\times10^{-9}}{6.63\times10^{-34}\times3\times10^{8}}$$

$$=1998.49\times10^{17}=1.998\times10^{20}$$

$$\Rightarrow \quad \approx 2\times10^{20} \Rightarrow x=2$$

$\therefore$ Answer is 2.

25 The number of photons emitted by a monochromatic (single frequency) infrared range finder of power 1 mW and wavelength of 1000 nm, in 0.1 second is $x\times10^{13}$. The value of x is ..... . (Nearest integer)

($h=6.63\times10^{-34}$ Js, $c=3.00\times10^{8}\ \text{ms}^{-1}$) **[2021, 27 Aug Shift-II]**

Ans. ***(50)***

Power of the source = 1 mW = 10^{-3} W

Energy of one photon, $E=h\nu=\frac{hc}{\lambda}$

where, $h=6.6\times10^{-34}$ Js,
$c=3\times10^{8}$ m/s and
$\lambda=1000$ nm
$=1000\times10^{-9}$ m ($1\text{nm}=10^{-9}$ m)
$=10^{-6}$ m

$$E=\frac{6.6\times10^{-34}\times3\times10^{8}}{10^{-6}}$$

$$\cong 20\times10^{-20}\ \text{J}$$

Power = number of photons emitted in one second × energy of 1 photon.

$$10^{-3}=n\times20\times10^{-20}$$

$$\Rightarrow \quad n=\frac{10^{-3}}{20\times10^{-20}}$$

$$=0.5\times10^{16}$$

Number of photons emitted in 1 s $=0.5\times10^{16}$

Number of photons emitted in 0.1 s $=0.5\times10^{16}\times0.1=50\times10^{13}$

$$x\times10^{13}=50\times10^{13}$$

$$x=50$$

26 A metal surface is exposed to 500 nm radiation. The threshold frequency of the metal for photoelectric current is 4.3×10^{14} Hz. The velocity of ejected electron is ..... $\times10^{5}\ \text{ms}^{-1}$. (Nearest integer)

[Use $h=6.63\times10^{-34}$ Js, $m_e=9.0\times10^{-31}$ kg] **[2021, 26 Aug Shift-II]**

Ans. ***(5)***

According to photoelectric effect

$$=\frac{hc}{\lambda}=h\nu_0+\frac{1}{2}mv^2$$

(where, h = Planck's constant,
λ = wavelength
ν_0 = threshold frequency,
v = velocity of electron
m = mass of electron,
c = speed of light)

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$$\Rightarrow \frac{6.63\times10^{-34}\times3\times10^{8}}{500\times10^{-9}}$$

$$=6.63\times10^{-34}\times4.3\times10^{14}+\frac{1}{2}mv^2$$

$$\frac{6.63\times30\times10^{-19}}{50}=6.63\times4.3\times10^{-20}+\frac{1}{2}mv^2$$

$$11.271\times10^{-20}\text{ J}=\frac{1}{2}\times9\times10^{-31}\times v^2$$

$$v=5\times10^{5}\text{ m/s}$$

$$\therefore \quad x=5$$

27 Given below are two statements :

Statement I Rutherford's gold foil experiment cannot explain the line spectrum of hydrogen atom.

Statement II Bohr's model of hydrogen atom contradicts Heisenberg's uncertainty principle.

In the light of the above statements, choose the most appropriate answer from the options given below :

[2021, 27 July Shift-I]

(a) Statement I is false but statement II is true.

(b) Statement I is true but statement II is false.

(c) Both statement I and statement II are false.

(d) Both statement I and statement II are true.

Ans. ***(d)***

Both Statement I and Statement II are true.

Rutherford proposed the nuclear model of the atom by gold foil experiment which showed that the atom is mostly empty space with tiny, dense, positively charged nucleus and electrons are continuously moving around nucleus but did not explain the line spectrum of hydrogen atom.

Definite line in H-spectrum are explained by Bohr.

Bohr's model of an atom is contradicted by Heisenberg uncertainty principle.

According to Bohr model, an electron in an atom is located at definite distance from nucleus and is revolving with definite velocity around it. While uncertainty principle explain that it is impossible to determine simultaneously exact position and velocity of electron.

28 An accelerated electron has a speed of $5\times10^{6}\text{ ms}^{-1}$ with an uncertainty of 0.02%. The uncertainty in finding its location while in motion is $x\times10^{-9}$ m. The value of x is ..... . (Nearest integer)

[Use mass of electron $=9.1\times10^{-31}$ kg, $h=6.63\times10^{-34}$ Js, $\pi=3.14$]

[2021, 25 July Shift-II]

Ans. ***(58)***

Uncertainity in speed of electron

$$=\Delta v=\frac{0.02}{100}\times5\times10^{6}$$

$$=10^{3}\text{ m/s}$$

Uncertainity in position $=x\times10^{-9}$ m

According to Heisenberg uncertainty principle,

$$\Delta x\cdot\Delta P=\frac{h}{4\pi m}$$

here, Δx = uncertainty in position

ΔP = uncertainty of momentum

h = Planck's constant

$\pi=\frac{22}{7}$ or 3.14

m = mass of electron

$$x\times10^{-9}\times10^{3}=\frac{6.626\times10^{-34}}{4\times3.14\times9.1\times10^{-31}}$$

$$x\times10^{-6}=0.058\times10^{-3}$$

$$\Rightarrow \quad x=\frac{0.058\times10^{-3}}{10^{-6}}=58$$

29 A source of monochromatic radiation of wavelength 400 nm provides 1000 J of energy in 10 seconds. When this radiation falls on the surface of sodium, $x\times10^{20}$ electrons are ejected per second. Assume that wavelength 400 nm is sufficient for ejection of electron from the surface of sodium metal. The value of x is ..... . (Nearest integer)

($h=6.626\times10^{-34}$ Js)

[2021, 25 July Shift-I]

Ans. ***(2)***

Total energy provided by source per second

$$=\frac{1000}{10}=100\text{ J}$$

Wavelength, $(\lambda)=400$ nm or 400×10^{-9} m

Planck's constant,

$h=6.626\times10^{-34}$ Js

Speed of light, $c=3\times10^{8}$ m/s

So, energy required to eject the electrons $E_{req}=\frac{hc}{\lambda}$

$$=\frac{6.626\times10^{-34}\text{ Js}\times3\times10^{8}\text{ ms}^{-1}}{400\times10^{-9}\text{ m}}$$

Number of ejected electrons $=\frac{100}{E_{req}}$

$$=\frac{100}{\frac{6.626\times10^{-34}\times3\times10^{8}}{400\times10^{-9}}}$$

$$=\frac{400\times10^{-7}\times10^{26}}{6.626\times3}$$

$$=\frac{40\times10^{-20}}{6.626\times3}$$

$$=2.01\times10^{20}$$

$$\simeq 2\times20^{20}$$

So, value is 2×10^{20} and x is 2.

30 The wavelength of electrons accelerated from rest through a potential difference of 40 kV is $x\times10^{-12}$ m. The value of x is ..... (Nearest integer)

Given : Mass of electron $=9.1\times10^{-31}$ kg

Charge on an electron $=1.6\times10^{-19}$ C

Planck's constant $=6.63\times10^{-34}$ Js

[2021, 20 July Shift-II]

Ans. ***(6)***

De-broglie wavelength of electron :

$$\lambda_e=\frac{h}{\sqrt{2m(\text{KE})}}$$

where λ_e = wavelength of electron

KE = kinetic energy of electron

also, kinetic energy $=qV$

q = charge of electron,

m = mass of electron,

V = potential.

$$\lambda_e=\frac{6.63\times10^{-34}}{\sqrt{2\times1.6\times10^{-19}\times9.1\times10^{-31}\times40\times10^{3}}}$$

$$\lambda_e=6.14\times10^{-12}\text{ m}$$

$$\therefore \quad x=6\text{(nearest)}$$

or

According to de-Broglie wavelength equation for electron,

$$\lambda=\frac{12.3}{\sqrt{V}}\text{ Å where, } V=\text{Voltage}$$

$$=\frac{12.3}{200}=6.15\times10^{-12}\text{m}$$

$$x\approx6$$

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31 When light of wavelength 248 nm falls on a metal of threshold energy 3.0 eV, the de- Broglie wavelength of emitted electrons is ..... Å.
[Round off to the nearest integer]
[Use: $\sqrt{3}=1.73$, $h=6.63\times10^{-34}$ Js
$m_e=9.1\times10^{-31}$ kg,
$c=3.0\times10^{8}\,ms^{-1}$, $1eV=1.6\times10^{-19}$ J]

[2021, 16 March Shift-I]

Ans. ***(9)***

Given wavelength, if incident light
$(\lambda)=248\,nm=2480$ Å
Threshold energy = 3.0 eV
We know, for electron de-Broglie wavelength is given by

$$\lambda=\frac{h}{mv}$$

$$\lambda=\frac{h}{\sqrt{2m(KE)}}$$

$KE=q\times V$ (where, q = charge of particle)
V = voltage applied

$$\lambda=\frac{h}{\sqrt{2m(qV)}}$$

Putting mass of electron,
$m_e=9.1\times10^{-31}$ kg
Charge of electron, $q=1.6\times10^{-19}$ C

$$\lambda=\sqrt{\frac{150}{V}}\text{ Å} \qquad ...(i)$$

We know,

$$E_{applied}=\phi+KE_{max} \qquad ...(ii)$$

where,
ϕ = threshold energy
$\phi=3$ eV

$$E_{applied}=\frac{12400}{\lambda_{Å}}=\frac{12400}{2480}=5\text{ eV}$$

Putting value in Eq. (ii),

$$5=3+KE_{max}$$

$$\Rightarrow \quad KE_{max}=2\text{ eV}$$

Voltage = 2

$$\lambda_e=\sqrt{\frac{150}{2}}=8.6\text{ Å} \qquad [\text{Eq. (i)}]$$

Nearest integer = 9

32 A ball weighing 10 g is moving with a velocity of 90 ms^{-1}. If the uncertainity in its velocity is 5%, then the uncertainty in its position is ..... $\times10^{-33}$ m (Rounded off to the nearest integer). [Given, $h=6.63\times10^{-34}$ J-s]

[2021, 26 Feb Shift-II]

Ans. ***(1)***

According to Heisenberg's uncertainty equation,

$$\Delta x\times m\Delta v\geq\frac{h}{4\pi} \qquad (\therefore m=10\text{ g}=10\times10^{-3}\text{ kg}, v=90\,ms^{-1})$$

Uncertainty in position,

$$\Delta x=\frac{h}{4\pi}\times\frac{1}{m\times\Delta v(\text{with uncertainty})}$$

$$=\frac{6.63\times10^{-34}}{4\times3.14}\times\frac{1}{(10\times10^{-3})\times\left(90\times\frac{5}{100}\right)}\text{ m}$$

$$=1.17\times10^{-33}\text{ m}\simeq1\times10^{-33}\text{ m}$$

33 A proton and a Li^{3+} nucleus are accelerated by the same potential. If λ_{Li} and λ_P denote the de-Broglie wavelengths of Li^{3+} and proton respectively, then the value of $\frac{\lambda_{Li}}{\lambda_P}$ is $x\times10^{-1}$. The value of x is ..... .
(Rounded off to the nearest integer)
(Mass of Li^{3+} = 8.3 mass of proton)

[2021, 24 Feb Shift-I]

Ans. ***(2)***

Given, mass of Li^{3+} = 8.3 times of mass of proton formula,
De-Broglie wavelength,

$$\lambda=\frac{h}{\sqrt{2mqV}}$$

Here, h = Planck's constant
$=6.624\times10^{-34}$ J-s
m = Mass of atom
q = Charge (or number of electrons)

$$\lambda_{Li}=\frac{h}{\sqrt{2m_{Li}(3e)v}} \qquad ...(i)$$

$$\lambda_P=\frac{h}{\sqrt{2m_P(e)v}} \qquad ...(ii)$$

Now, Eq. (i) divided by Eq. (ii), we get,

$$\frac{\lambda_{Li}}{\lambda_P}=\sqrt{\frac{m_P(e)v}{m_{Li}(3e)v}}$$

We know that $m_{Li}=8.3\,m_p$

$$\frac{\lambda_{Li}}{\lambda_P}=\sqrt{\frac{m_P\times e\times V}{8.3\,m_P\times3e\times V}}$$

$$=\sqrt{\frac{1}{8.3\times3}}=\frac{1}{5}=0.2$$

$$=2\times10^{-1}$$

Hence, $x\times10^{-1}$, $x=2$

34 The work function of sodium metal is 4.41×10^{-19} J. If photons of wavelength 300 nm are incident on the metal, the kinetic energy of the ejected electrons will be
($h=6.63\times10^{-34}$ J s; $c=3\times10^{8}$ m/s)
..... $\times10^{-21}$ J.

[2020, 2 Sep Shift-II]

Ans. ***(222)***

For photoelectrons, its kinetic energy will be

$$KE=E-E_a=\frac{hc}{\lambda}-E_0$$

$$=\frac{6.63\times10^{-34}\times3\times10^{8}}{300\times10^{-9}}-4.41\times10^{-19}\text{ J}$$

$$=222\times10^{-21}\text{ J}$$

λ = Wavelength of photon
$=300\text{ nm}=300\times10^{-9}$ m
E_0 = Threshold energy
= Work function of sodium metal
$=4.41\times10^{-19}$ J

35 The de Broglie wavelength of an electron in the 4th Bohr orbit is

[2020, 9 Jan Shift-I]

(a) $6\pi a_0$ (b) $2\pi a_0$ (c) $8\pi a_0$ (d) $4\pi a_0$

Ans. ***(c)***

The de-Broglie wavelength of an electron,

$$\lambda=\frac{h}{p},\text{ or }\frac{h}{mv}$$

But, from the Bohr's postulate of quantisation of angular momentum of electrons, $l=mvr=\frac{nh}{2\pi}$,

$$\therefore \qquad mv=\frac{nh}{2\pi r}$$

Upon substitution, $\lambda=\frac{h}{\left(\frac{nh}{2\pi r}\right)}=\frac{2\pi r}{n}$,

where, r is the radius of orbits in Bohr model $=\frac{n^2a_0}{Z}$

$$\therefore\ \lambda=\frac{2\pi\times n^2\times a_0}{n\times Z}=\frac{2\pi na_0}{Z}=8\pi a_0$$

$\{Z=1$ for hydrogen, $n=4$ (given)$\}$

36 What is the work function of the metal, if the light of wavelength 4000 Å generates photoelectron of velocity $6\times10^{5}\,ms^{-1}$ from it?
(Mass of electron $=9\times10^{-31}$ kg
Velocity of light $=3\times10^{8}\,ms^{-1}$
Planck's constant $=6.626\times10^{-34}$ Js
Charge of electron
$=1.6\times10^{-19}$ JeV^{-1})

(a) 4.0 eV (b) 2.1 eV (c) 0.9 eV (d) 3.1 eV

[2019, 12 Jan Shift-I]

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Ans. ***(b)***

Work function of metal $(\phi) = h\nu_0$

where, ν_0 = threshold frequency

Also, $\frac{1}{2}m_e v^2 = h\nu - h\nu_0$

or $\frac{1}{2}m_e v^2 = h\nu - \phi$ ...(i)

$\frac{1}{2}m_e v^2 = \frac{hc}{\lambda} - \phi$ ...(ii)

Given : $\lambda = 4000\ \text{Å} = 4000 \times 10^{-10}\text{m}$

$v = 6 \times 10^5\ \text{ms}^{-1}$,

$m_e = 9 \times 10^{-31}\ \text{kg}$, $c = 3 \times 10^8\ \text{ms}^{-1}$

$h = 6.626 \times 10^{-34}\ \text{Js}$

Thus, on substituting all the given values in Eq. (i), we get

$$\frac{1}{2} \times 9 \times 10^{-31}\ \text{kg} \times (6 \times 10^5\ \text{ms}^{-1})^2 = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3 \times 10^8\ \text{ms}^{-1}}{4000 \times 10^{-10}\text{m}} - \phi$$

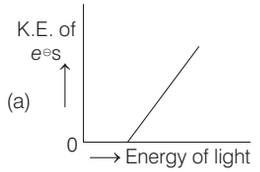
$\therefore \phi = 1.62 \times 10^{-21}\ \text{kgm}^2\text{s}^{-2} - 4.96 \times 10^{-19}\ \text{J}$

$= 3.36 \times 10^{-19}\ \text{J}$ $[1\ \text{kg m}^2\text{s}^{-2} = 1\ \text{J}]$

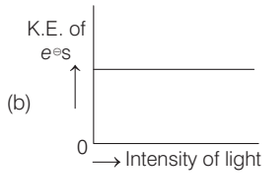
$= 2.1\ \text{eV}$

37 Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface? **[2019, 10 Jan Shift-I]**

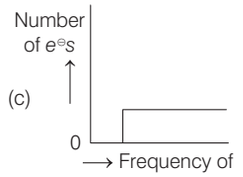
(a)



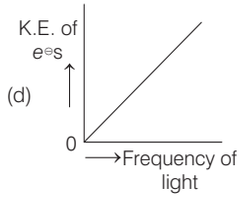
(b)



(c)



(d)



Ans. ***(d)***

For photoelectric effect,

(i) $KE = E - E_0$

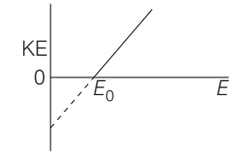
where, KE = Kinetic energy of ejected electrons.

E = Energy of incident light $= h\nu$

E_0 = Threshold energy $= h\nu_0$

ν = Frequency of incident light

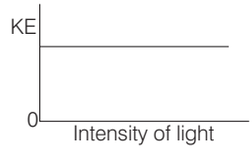
ν_0 = Threshold frequency



Slope $= \pm 1$, intercept $= -E_0$

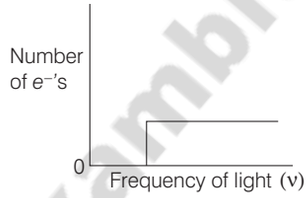
So, option (a) is correct.

(ii) KE of ejected electrons does not depend on the intensity of incident light.



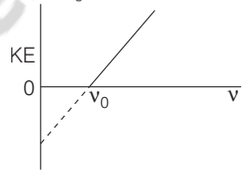
So, option (b) is correct.

(iii) When, number of ejected electrons is plotted with frequency of light, we get



So, option (c) is also correct.

(iv) $KE = h\nu - h\nu_0$



Slope $= +h$, intercept $= -h\nu_0$

So, option (d) is not correct.

38 If p is the momentum of the fastest electron ejected from a metal surface after the irradiation of light having wavelength λ, then for 1.5 p momentum of the photoelectron, the wavelength of the light should be

(Assume kinetic energy of ejected photoelectron to be very high in comparison to work function)

[2019, 8 April Shift-II]

(a) $\frac{4}{9}\lambda$ (b) $\frac{3}{4}\lambda$

(c) $\frac{2}{3}\lambda$ (d) $\frac{1}{2}\lambda$

Ans. ***(a)***

The expression of kinetic energy of photo electrons,

$$KE = \frac{1}{2}mv^2 = E - E_0$$

When, $KE >> E_0$, the equation becomes,

$$KE = \frac{1}{2}mv^2 = E$$

$$\Rightarrow \quad \frac{1}{2}mv^2 = \frac{hc}{\lambda} \Rightarrow \frac{p^2}{2m^2} = \frac{hc}{\lambda}$$

$$\Rightarrow \lambda = hc \times 2m^2 \times \frac{1}{p^2} \Rightarrow \lambda \propto \frac{1}{p^2}$$

$E = \frac{hc}{\lambda}$ = energy of incident light.

E_0 = threshold energy or work functions,

$$\frac{1}{2}mv^2 = \frac{1}{2} \times \frac{(mv)^2}{m^2} = \frac{1}{2} \times \frac{p^2}{m^2}$$

$\because p$ = momentum $= mv$

As per the given condition,

$$\frac{\lambda_2}{\lambda_1} = \left(\frac{p_1}{p_2}\right)^2$$

$$\Rightarrow \quad \frac{\lambda_2}{\lambda} = \left(\frac{p}{1.5 \times p}\right)^2 = \left(\frac{2}{3}\right)^2 = \frac{4}{9}$$

$$\Rightarrow \quad \lambda_2 = \frac{4}{9}\lambda \qquad \left[\because \lambda_1 = \lambda,\ p_1 = p\right]$$

39 The de-Broglie wavelength (λ) associated with a photoelectron varies with the frequency (ν) of the incident radiation as,

[ν_0 is threshold frequency]

(a) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{4}}}$ (b) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{3}{2}}}$

(c) $\lambda \propto \frac{1}{(\nu - \nu_0)}$ (d) $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{2}}}$

[2019, 11 Jan Shift-II]

Ans. ***(d)***

de-Broglie wavelength (λ) for electron is given by

$$\lambda = \frac{h}{\sqrt{2\,m\,K.E}} \quad \text{...(i)}$$

Also, according to photoelectric effect

$$KE = h\nu - h\nu_0$$

On substituting the value of KE in Eq (i), we get

$$\lambda = \frac{h}{\sqrt{2m \times (h\nu - h\nu_0)}} \Rightarrow \lambda \propto \frac{1}{(\nu - \nu_0)^{1/2}}$$

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40 If the de-Broglie wavelength of the electron in n^{th} Bohr orbit in a hydrogenic atom is equal to $1.5\pi a_0$ (a_0 is Bohr radius), then the value of n/Z is

(a) 1.0 (b) 0.75 (c) 0.40 (d) 1.50

[2019, 12 Jan Shift-II]

Ans. ***(b)***

$$\text{Number of waves} = \frac{\text{Circumference}}{\text{Wavelength}}$$

$$n = \frac{2\pi r}{\lambda} \Rightarrow 2\pi r = n\lambda \quad \ldots(i)$$

Also, we know that radius (r) of an atom is given by

$$r = \frac{a_0 n^2}{Z}$$

Thus, Eq. (i) becomes

$$2\pi a_0 \frac{n^2}{Z} = n\lambda \quad \ldots(ii)$$

$$\therefore \quad 2\pi a_0 \frac{n^2}{Z} = n(1.5\,\pi a_0)$$

[Given, $\lambda = 1.5\,\pi a_0$]

$$\frac{n}{Z} = \frac{1.5\pi a_0}{2\pi a_0} = \frac{1.5}{2} = 0.75$$

41 A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron, respectively, then the value of h/λ (where, λ is wavelength associated with electron wave) is given by **[JEE Main 2016]**

(a) $2\,meV$ (b) $\sqrt{meV}$

(c) $\sqrt{2\,meV}$ (d) meV

Ans. ***(c)***

As you can see in options, energy term is mentioned hence, we have to find out relation between $\frac{h}{\lambda}$ and energy. For this, we shall use de-Broglie wavelength and kinetic energy term in eV.

de-Broglie wavelength for an electron

$$(\lambda) = \frac{h}{p}$$

$$\Rightarrow \quad p = \frac{h}{\lambda} \quad \ldots(i)$$

Kinetic energy of an electron = eV

As we know that, $KE = \frac{p^2}{2m}$

$$\therefore \quad eV = \frac{p^2}{2m} \text{ or } p = \sqrt{2meV} \quad \ldots(ii)$$

From equations (i) and (ii), we get

$$\frac{h}{\lambda} = \sqrt{2meV}$$

TOPIC 4
Quantum Mechanical Model

42 The value of magnetic quantum number of the outermost electron of Zn^+ ion is **[2021, 31 Aug Shift-II]**

Ans. ***(0)***

The configuration of

$Zn^+ = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

The outermost electron is in s-orbital.

For s-orbital, azimuthal quantum number (l) = 0

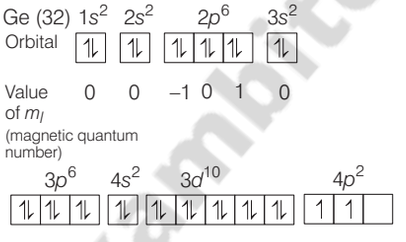
Magnetic quantum number, $m = -l$ to $+l$

For $l = 0$, $m = 0$

43 Ge ($Z = 32$) in its ground state electronic configuration has x completely filled orbitals with $m_l = 0$. The value of x is **[2021, 31 Aug Shift-I]**

Ans. ***(7)***

Ge ($Z = 32$) electronic configuration is



For s-orbitals (1s, 2s, 3s and 4s) $m_l = 0$ {2 × 0}

For p-orbitals (2p, 3p) $m_l = 0$

{(−1) × 2 + 0 × 2 + (+1) × 2 = 0}

For d-orbitals (3d) $m_l = 0$

$$\left\{\begin{matrix}(-2)\times 2 + (-1)\times 2 + 0\times 2 \\ (+1)\times 2 + (+2)\times 2 = 0\end{matrix}\right\}$$

∴ Completely filled orbitals with $m_l = 0$ are seven (7).

44 A certain orbital has no angular nodes and two radial nodes. The orbital is **[2021, 18 March Shift-I]**

(a) 2s (b) 3s

(c) 3p (d) 2p

Ans. ***(b)***

As, we know,

For 2s orbital, $n = 2, l = 0$

Angular node (l) = 0

Radial nodes = $n - l - 1$

$\Rightarrow \quad 2 - 0 - 1 = 1$

For 2p orbital, $n = 2$ and $l = 1$

Angular node (l) = 1

Therefore, number of radial nodes

$= 2 - 1 - 1 = 0$

It has one angular and zero radial node.

For 3p orbital, $n = 3, l = 1$

Angular node (l) = 1

It has one angular and one radial node.

For 3s orbital, $n = 3, l = 0$

No. of angular node (l) = 0

No. of radial node $\Rightarrow n - l - 1$

$= 3 - 0 - 1 = 2 = 2$

Hence, for 3s-orbital has no angular node and 2 radial nodes.

45 A certain orbital has $n = 4$ and $m_l = -3$. The number of radial nodes in this orbital is ..... (Round off to the nearest integer).

[2021, 17 March Shift-I]

Ans. ***(0)***

Given, $n = 4$, $m_l = -3$, so $l = 3$

Possible value of $l = 0, 1, 2, 3$

As $m = -3$ is possible only for $l = 3$

For $l = 3$, $m_l = -3, -2, -1, 0, 1, 2, 3$

So, this is 4f-orbital.

Number of radial nodes = $n - l - 1$

$= 4 - 3 - 1 = 0$

So, there is no radial node in 4f orbital.

46 The number of orbitals with $n = 5$, $m_l = +2$ is ..... . (Round off to the nearest integer).

[2021, 16 March Shift-II]

Ans. ***(3)***

Given, $n = 5$, $m_l = +2$

For $n = 5$, possible value of $l = 0, 1, 2, 3, 4$

For $l = 0$, $m_l = 0$

$l = 1$, $m_l = -1, 0, 1$

$l = 2$, $m_l = -2, -1, 0, 1, 2$

$l = 3$, $m_l = -3, -2, -1, 0, 1, 2, 3$

$l = 4$, $m_l = -4, -3, -2, -1, 0, 1, 2, 3, 4$

Possible value of m_l for a given value of l

$= 0, \pm 1, \pm 2, \pm 3 \ldots . \pm l$

So, number of orbitals having $n = 5$ and $m_l = \pm 2$ are 3.

47 Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) In TlI_3, isomorphous to CsI_3, the metal is present in +1 oxidation state.

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Reason (R) Tl metal has fourteen *f*-electrons in the electronic configuration.

In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 26 Feb Shift-II]

(a) A is correct but R is not correct.
(b) Both A and R are correct and R is the correct explanation of A.
(c) A is not correct but R is correct
(c) Both A and R are correct but R is not correct explanation of A.

Ans. ***(b)***

Assertion (A) is correct. TlI_3 and CsI_3 are the triiodide, I_3^- (polyhalide) compounds of Tl^+ and Cs^+ ions. Due to inert pair effect of group -13 elements, Tl^+ is more stable than Tl^{3+}. Cs and Tl belong to the same period (6th).

Sizes of Cs^+ and Tl^+ are nearly same.

So, geometrical network and lattice pattern of both CsI_3 and TlI_3 are same (bcc lattice). CsI_3 and TlI_3 are also able to form mixed crystals when crystallisation is carried out from a mixture of saturated solutions of CsI_3 and TlI_3. These properties enable TlI_3 and CsI_3 to be isomorphous crystals.

Reason (R) is also correct. Electronic configuration of Cs ($Z = 55$) and Tl ($Z = 81$) as follows

$_{55}Cs : [_{54}Xe]6s^1$

$_{81}Tl : [_{54}Xe]4f^{14}5d^{10}6s^26p^1$

So, Tl has fourteen *f*-electrons in the anti-penultimate (4th) shell.

A and R are individually correct and R is the correct explanation of A.

48 The orbital having two radial as well as two angular nodes is

[2021, 26 Feb Shift-I]

(a) 3*p* (b) 4*f* (c) 4*d* (d) 5*d*

Ans. ***(d)***

Number of radial nodes = $(n - l - 1)$

[n = principal quantum number, l = azimuthal quantum number]

Number of angular nodes = l

	$(n-l-1)$		l
(a) 3*p* ($n = 3, l = 1$)	$\Rightarrow$	1	1
(b) 4*f* ($n = 4, l = 3$)	$\Rightarrow$	0	3
(c) 4*d* ($n = 4, l = 2$)	$\Rightarrow$	1	2
(d) 5*d* ($n = 5, l = 2$)	$\Rightarrow$	2	2

So, 5*d*-orbital has two radial as well as two angular nodes (option-d).

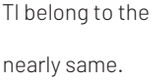
Note $l = 0$ for *s*-orbital, $l = 1$ for *p*-orbital, $l = 2$ for *d*-orbital and $l = 3$ for *f*-orbital.

49 The spin only magnetic moment of a divalent ion in aqueous solution (atomic number = 29) is ..... BM.

[2021, 25 Feb Shift-II]

Ans. ***(2)***

$Z = 29\,[Cu] \xrightarrow{-2e^-} Cu^{2+} = [Ar]3d^9$

$3d^9 =$ 

Number of unpaired electron, $n = 1$

$\therefore$ Spin only magnetic moment,

$\mu = \sqrt{n(n+2)}\,BM$

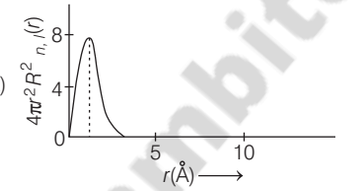
$= \sqrt{1(1+2)}\ BM$

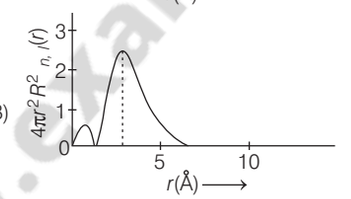
$= \sqrt{3}\ BM$

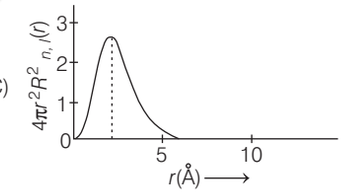
$= 1.73\ BM \simeq 2\ BM$

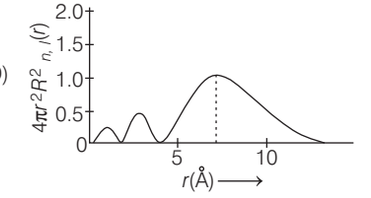
50 The plots of radial distribution functions for various orbitals of hydrogen atom against '*r*' are given below.

[2021, 25 Feb Shift-I]

(A) 

(B) 

(C) 

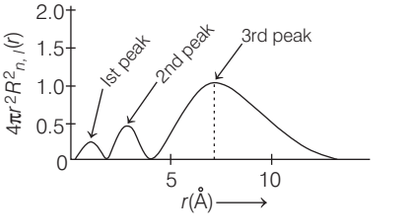
(D) 

The correct plot for 3*s*-orbital is

(a) (A) (b) (B) (c) (C) (d) (D)

Ans. ***(d)***

The correct plot for 3*s*-orbital is



For 3*s*,

value of $l = 0$

value of $n = 3$

Number of peak = $n - l = 3 - 0 = 3$

In graph *D*, three peaks are present, so this is the correct plot for 3*s*-orbital.

51 The number of subshells associated with $n = 4$ and $m = -2$ quantum numbers is

[2020, 2 Sep Shift-II]

(a) 8 (b) 2 (c) 16 (d) 4

Ans. ***(b)***

Principal quantum number (n) signifies the shell or orbit number.

From the number of values of azimuthal quantum number (l), we can calculate number of subshells present in a shell as,

$l = 0 \ldots (n-1)$

So, when $n = 4$

The permissible values of l and subshells are

$l = 0 \rightarrow s$-subshell

$= 1 \rightarrow p$-subshell

$= 2 \rightarrow d$-subshell

$= 3 \rightarrow f$-subshell

But, here values of l are restricted by the value of magnetic quantum number, $m = -2$, where, m depends on l as

$m = -l \ldots 0 \ldots +l$

So, $m = -2$ value is possible for two subshells, viz, $l = 3$ (*f*-subshell) and $l = 2$ (*d*-subshell) only.

$l = 3 \Rightarrow m = -3, -2, -1, 0, +1, +2, +3$

$l = 2 \Rightarrow m = -2, -1, 0, +1, +2$

52 Consider the hypothetical situation where the azimuthal quantum number, l takes values 0, 1, 2, ... $n+1$, where n is the principle quantum number. Then, the element with atomic number

[2020, 3 Sep Shift-II]

(a) 8 is the first noble gas
(b) 13 has a half-filled valence subshell
(c) 9 is the first alkali metal
(d) 6 has a 2*p*-valence subshell

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Ans. ***(b)***

Hypothetical situation :

Azimuthal quantum number $(l) = 0 - (n-1)$

n = Principal quantum number

For, $n = 1$ $\quad l = 0, \ 1, \ 2$

$\downarrow \ \downarrow \ \downarrow$

$1s \ \ 1p \ \ 1d$

$1s^2 \ \ 1p^6 \ \ 1d^{10}$

Number of electrons in s-orbital = 2

Number of electrons in p-orbital = 6

Number of electrons in d-orbital = 10

$Z = 13$ (Half-filled valence sub-shell)

For $n = 1$, $1s^2\,1p^6\,1d^5$ ($Z = 13$)

Number of electrons in 1d-orbital are 5. (It is half-filled).

Element with atomic number 9 is not first alkali metal but a halogen $1s^2 2s^2 2p^5$.

First noble gas has atomic number 2 not 8.

53 The correct statement about probability density (except at infinite distance from nucleus) is **[2020, 5 Sep Shift-II]**

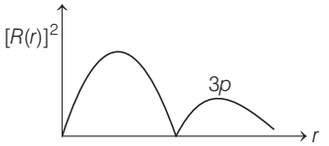
(a) it can be zero for 1s orbital

(b) it can be negative for 2p orbital

(c) it can be zero for 3p orbital

(d) it can never be zero for 2s orbital

Ans. ***(c)***



ϕ^2 (Probability density) can be zero for 3p orbital other than infinite distance.

Since, $n = 3$, $l = 1$ for 3p orbital, the number of radial nodes = 3 − 1 − 1 = 1

54 The number of orbitals associated with quantum numbers $n = 5$, $m_s = +\frac{1}{2}$ is **[2020, 7 Jan Shift-I]**

(a) 25 (b) 50 (c) 15 (d) 11

Ans. ***(a)***

According to quantum mechanical atom model, for each value of n (principal quantum number), there are 'n' different values of l (azimuthal quantum number), i.e. $l = 0, 1, 2, \ldots, (n-1)$. And, for each value of l, there are $2l + 1$ different values of m_l (magnetic quantum number), i.e. $m_l = 0, \pm1, \pm2 \ldots \pm l$.

∴ Total number of possible combinations of n, l and m_l, for a given value of n is n^2, and each such combination is associated with an orbital. Each orbital can occupy a maximum of two electrons, having a different value of spin quantum number (m_s), which are $+\frac{1}{2}$ or $-\frac{1}{2}$.

∴ Number of orbitals associated with $n = 5$ is $n^2 = 25$. Each of those orbitals can be associated with $m_s = +\frac{1}{2}$ as well as $m_s = -\frac{1}{2}$.

∴ Answer = 25

55 The quantum number of four electrons are given below:

I. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$

II. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$

III. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$

IV. $n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}$

The correct order of their increasing energies will be **[2019, 8 April Shift-I]**

(a) IV < III < II < I (b) I < II < III < IV

(c) IV < II < III < I (d) I < III < II < IV

Ans. ***(c)***

Smaller the value of $(n+l)$, smaller the energy. If two or more sub-orbits have same values of $(n+l)$, sub-orbits with lower values of n has lower energy. The $(n+l)$ values of the given options are as follows :

I. $n = 4, l = 2$; $n+l = 6$

II. $n = 3, l = 2$; $n+l = 5$

III. $n = 4, l = 1$, $n+l = 5$

IV. $n = 3, l = 1$, $n+l = 4$

Among II and III, $n = 3$ has lower value of energy. Thus, the correct order of their increasing energies will be

IV < II < III < I

56 Which one of the following about an electron occupying the 1s-orbital in a hydrogen atom is incorrect? (The Bohr radius is represented by a_0) **[2019, 9 April Shift-II]**

(a) The electron can be found at a distance $2a_0$ from the nucleus.

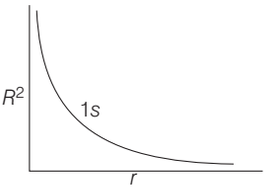
(b) The magnitude of the potential energy is double that of its kinetic energy on an average.

(c) The probability density of finding the electron is maximum at the nucleus.

(d) The total energy of the electron is maximum when it is at a distance a_0 from the nucleus.

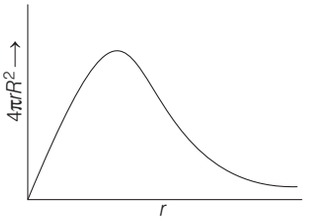
Ans. ***(d)***

Statement (d) is incorrect. For 1s-orbital radial probability density (R^2) against r is given as:



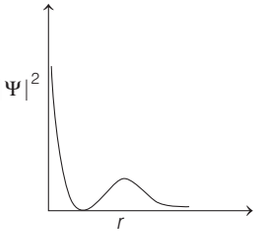
For 1s-orbital, probability density decreases sharply as we move away from the nucleus.

The radial distribution curves obtained by plotting radial probability functions *vs* r for 1s-orbital is



The graph initially increases and then decreases. It reaches a maximum at a distance very close to the nucleus and then decreases. The maximum in the curve corresponds to the distance at which the probability of finding the electron in maximum.

57 The graph between $|\psi|^2$ and r (radial distance) is shown below. This represents **[2019, 10 April Shift-I]**



(a) 1s-orbital

(b) 2p-orbital

(c) 3s-orbital

(d) 2s-orbital

Ans. ***(d)***

The graphs between $|\psi|^2$ and r are radial density plots having $(n-l-1)$ number of radial nodes. For 1s, 2s, 3s and 2p-orbitals these are respectively.

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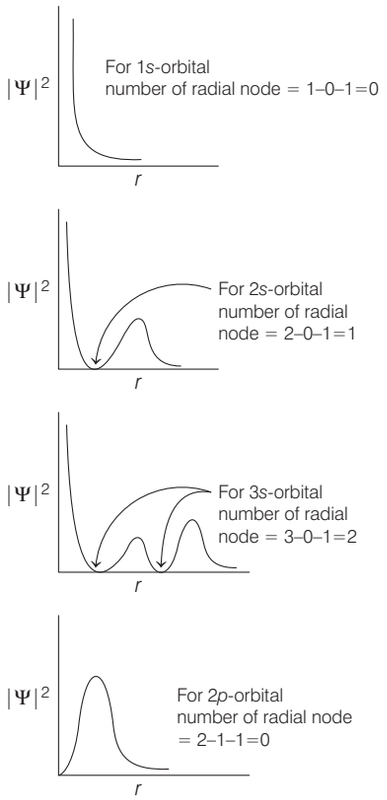
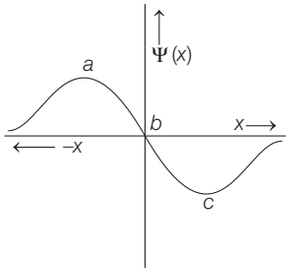


Thus, the given graph between $|\psi|^2$ and r represents 2s-orbital.

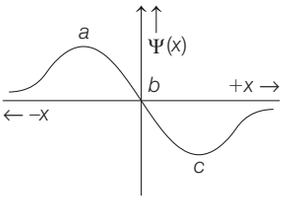
58 The electrons are more likely to be found **[2019, 12 April Shift-I]**



(a) in the region a and c
(b) in the region a and b
(c) only in the region a
(d) only in the region c

Ans. ***(a)***

The electrons are more likely to be found in the region a and c. At b, wave function becomes zero and is called radial nodal surface or simply node.



The graph between wavefunction (ψ) and distance (r) from the nucleus helps in determining the shape of orbital.

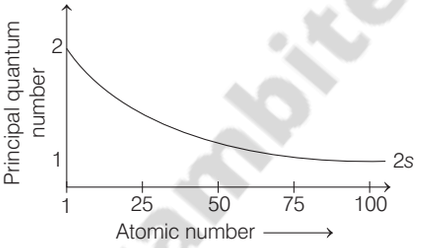
59 Among the following, the energy of 2s-orbital is lowest in **[2019, 12 April Shift-II]**

(a) K (b) H (c) Li (d) Na

Ans. ***(a)***

The energy of 2s-orbital is lowest in K(potassium). An orbital gets larger as the principal quantum number n increases.

Correspondingly, the energy of the electron in such an orbital becomes less negative, meaning that the electron is less strongly bound and has less energy. The graph of principal quantum number with atomic number is



60 Which of the following combination of statements is true regarding the interpretation of the atomic orbitals?

I. An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.
II. For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.
III. According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2\pi}$.
IV. The plot of ψ *vs* r for various azimuthal quantum numbers, shows peak shifting towards higher r value.

[2019, 9 Jan Shift-II]

(a) I, III (b) II, III
(c) I, II (d) I, IV

Ans. ***(d)***

(I) Angular momentum, $mvr = \frac{nh}{2\pi}$

$\Rightarrow mvr \propto n \propto$ distance from the nucleus

(II) This statement is incorrect as size of an orbit

$\propto$ Azimuthal quantum number (l)

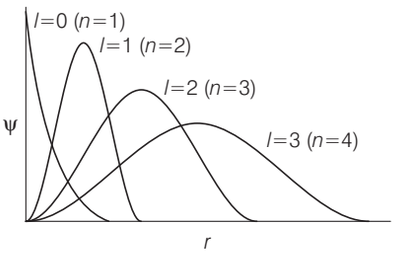
($\because n =$ constant)

(III) This statement is incorrect as at ground state,
$n = 1, l = 0$

$\Rightarrow$ Orbital angular momentum (wave mechanics)

$$= \sqrt{l(l+1)}\,\frac{h}{2\pi} = 0 \quad [\because l = 0]$$

(IV) The given plot is



61 The correct set of four quantum numbers for the valence electrons of rubidium atom [$Z = 37$] is **[JEE Main 2014]**

(a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
(c) $5, 1, 1, +\frac{1}{2}$ (d) $5, 0, 1, +\frac{1}{2}$

Ans. ***(a)***

The electronic configuration of rubidium atom ($Z = 37$) is given by

$$Rb = [Kr]\ 5s^1$$

Hence, the quantum numbers for $5s^1$ electron is given by

$$n = 5,\ l = 0,\ m = 0,$$
$$s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

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04

Chemical Bonding and Molecular Structure

TOPIC 1

Type of Bonds, Bond Parameter and Resonance

01 The interaction energy of London forces between two particles is proportional to r^x, where r is the distance between the particles. The value of x is

[2021, 26 Aug Shift-II]

(a) 3 (b) – 3 (c) – 6 (d) 6

Ans. ***(c)***

In London forces, interaction energy in inversely proportional to the sixth power of the distance between two interacting particles ($1/r^6$ or r^{-6}).

$\therefore$ x is –6.

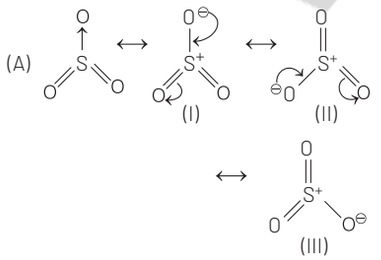
02 Identify the species having one π - bond and maximum number of canonical forms from the following

[2021, 25 July Shift-II]

(a) SO_3 (b) O_2
(c) SO_2 (d) CO_3^{2-}

Ans. ***(d)***

Canonical form of

(A) 

(I) (II) (III)

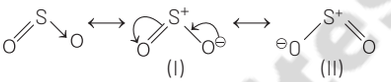
$\therefore SO_3$ has 2 π-bonds and has 3 number of canonical forms.

(B) O_2

$:\ddot{O}=\ddot{O}:$

$\therefore O_2$ has 1π-bond and has 1 structure.

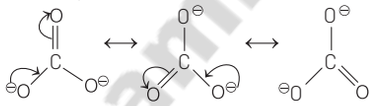
(C) SO_2



(I) (II)

$\therefore SO_2$ has 1π-bond and has 2 canonical forms.

(D) CO_3^{2-}



$\therefore$ CO_3^{2-} has 1π-bond and has 3 canonical forms.

Among SO_3, O_2, SO_2 and CO_3^{2-}, only CO_3^{2-} has only one π-bond and maximum number of canonical forms.

03 The set in which compounds have different nature is

[2021, 20 July Shift-I]

(a) $B(OH)_3$ and H_3PO_3
(b) $B(OH)_3$ and $Al(OH)_3$
(c) NaOH and $Ca(OH)_2$
(d) $Be(OH)_2$ and $Al(OH)_3$

Ans. ***(b)***

(a) Both are acidic in nature.

$B(OH)_3$ is orthoboric acid. It can accept a pair of electrons from Lewis bases and hence, act as Lewis acid.

H_3PO_3 is (phosphorus acid) diprotic acid as it readily ionises two protons.

(b) $B(OH)_3$ is acidic and $Al(OH)_3$ is amphoteric in nature.

(c) Both NaOH and $Ca(OH)_2$ are basic hydroxides.

(d) Both $Be(OH)_2$ and $Al(OH)_3$ are amphoteric hydroxides.

Hence, only $B(OH)_3$ and $Al(OH)_3$ have different nature.

04 Given below are two statements: One is labelled as Assertion (A) and the other is labelled as Reason (R).
Assertion (A) Dipole-dipole interactions are the only non-covalent interactions, resulting in hydrogen bond formation.
Reason (R) Fluorine is the most electronegative element and hydrogen bonds in HF are symmetrical.
In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 26 Feb Shift-I]

(a) A is false but R is true.
(b) Both A and R are true and R is the correct explanation of A.
(c) A is true R is false.
(d) Both A and R are true but R is not the correct explanation of A.

Ans. ***(a)***

Assertion is false but Reason is true.
Corrected Assertion Diple-dipole interactions are purely covalent interactions of dipolar covalent bonds.

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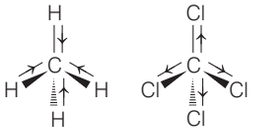
Ends of dipoles of a polar covalent bonds possess partial charges (δ^+ and δ^-) which are less than unit electronic charge, $e = 1.6\times10^{-19}$ C.

05 The dipole moments of CCl_4, $CHCl_3$ and CH_4 are in the order

[2020, 7 Jan Shift-I]

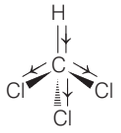
(a) $CCl_4 < CH_4 < CHCl_3$
(b) $CH_4 < CCl_4 < CHCl_3$
(c) $CH_4 = CCl_4 < CHCl_3$
(d) $CHCl_3 < CH_4 = CCl_4$

Ans. ***(c)***



CH_4 ($\mu=0$) CCl_4 ($\mu=0$)

Individual bonds have some dipole moment (μ), but overall $\mu=0$, due to mutual cancellation of dipole moments as the structures are symmetrical.



$CHCl_3$ ($\mu\neq0$)

The resultant of three C — Cl bond dipoles is not cancelled but enhanced by C — H bond dipole.

06 Match the type of interaction in column *A* with the distance dependence of their interaction energy in column *B* :

	A		*B*
(I)	Ion-ion	(a)	$\frac{1}{r}$
(II)	Dipole-dipole	(b)	$\frac{1}{r^2}$
(III)	London dispersion	(c)	$\frac{1}{r^3}$
		(d)	$\frac{1}{r^6}$

[2020, 2 Sep Shift-II]

(a)(I)-(b), (II)-(d), (III)-(c)
(b)(I)-(a), (II)-(b), (III)-(d)
(c)(I)-(a), (II)-(b), (III)-(c)
(d)(I)-(a), (II)-(c), (III)-(d)

Ans. ***(a)***

When *r* is the inter-nuclear separation,

(I) ion-ion interaction energy $\propto \frac{1}{r}$ [column -B(a)]

(II) dipole-dipole interaction energy $\propto \frac{1}{r^3}$ [column-B(c)](for stationary polar molecules)

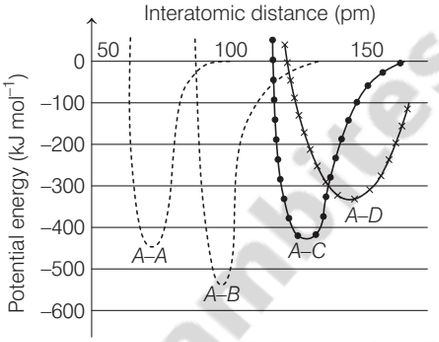
$\propto \frac{1}{r^6}$ [column-B(d)](for rotating polar molecules)

(III) London dispersion interaction energy $\propto \frac{1}{r^6}$ [column-B(d)]

[dipole induced dipole interaction energy $\propto \frac{1}{r^6}$]

So, the matching is,
(I)-(a), (II)-(c), (III)-(d)] option (a).

07 The intermolecular potential energy for the molecules *A*, *B*, *C* and *D* given below suggests that:



[2020, 4 Sep Shift-I]

(a) *A*-*B* has the stiffest bond
(b) *D* is more electronegative than other atoms
(c) *A*-*A* has the largest bond enthalpy
(d) *A*-*D* has the shortest bond length

Ans. ***(a)***

(a) *A*-*B* has stiffest bond.
This is correct because the potential energy of *A*-*B* has maximum negative value [between –500 to –600]. More negative is the potential energy means high energy is released. Higher the released energy higher is the stability and hence the stiffness bond.

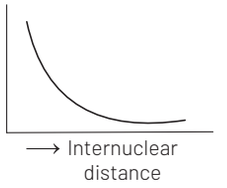
(b) *D* is more electronegative than other atoms, it is incorrect.

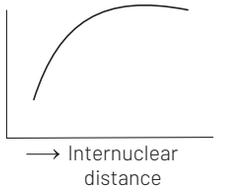
(c) *A*-*A* has the largest bond enthalpy, it is incorrect because value of potential energy is more negative in *A*-*B*.

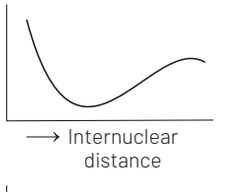
(d) *A*-*D* has shortest bond length, it is incorrect because inter molecular distance in between *A*-*D* more than 150 (pm) which is height in all.

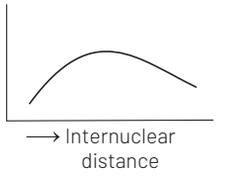
08 The potential energy curve for the H_2 molecule as a function of internuclear distance is

[2020, 5 Sep Shift-I]

(a)


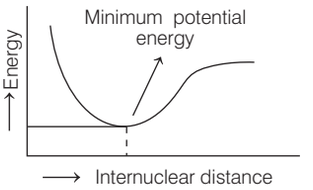
(b)


(c)


(d)


Ans. ***(c)***

When the distance of hydrogen nucleus is decreasing at a particular point, energy is minimum. At this point potential energy will be least. It is the point when bond formation taken place.



Hence, option (c) is correct.

09 Arrange the following bonds according to their average bond energies in descending order

C—Cl, C—Br, C—F, C—I

[2020, 8 Jan Shift-II]

(a) C—F > C—Cl > C—Br > C—I
(b) C—Br > C—I > C—Cl > C—F
(c) C—I > C—Br > C—Cl > C—F
(d) C—Cl > C—Br > C—I > C—F

Ans. ***(a)***

The correct descending order of bonds according to their average bond

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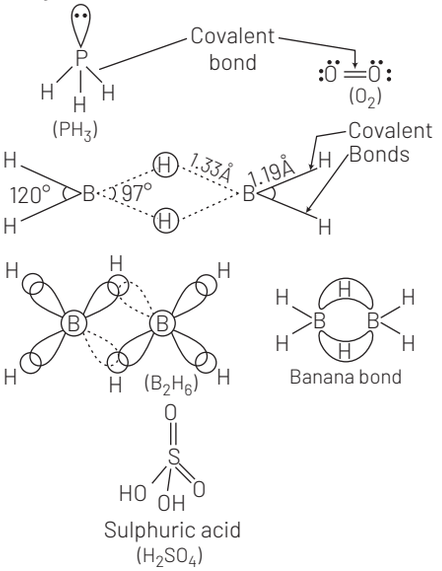
energies is as follows :
C—F > C—Cl > C—Br > C—I
Bond length is inversely proportional to bond energy. So, bond length decreases as bond energy increases.

10 Which of the following compounds contain(s) no covalent bond(s)?
KCl, PH_3, O_2, B_2H_6, H_2SO_4 **[JEE Main 2018]**

(a) KCl, B_2H_6, PH_3 (b) KCl, H_2SO_4
(c) KCl (d) KCl, B_2H_6

Ans. ***(c)***

KCl is the only ionic compound. The structure of PH_3, O_2, B_2H_6 and H_2SO_4 are given below



All bond between S and O atom are covalent bonds.

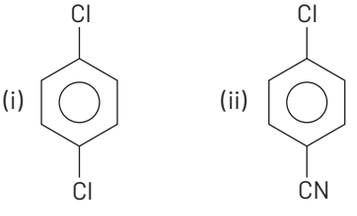
11 The correct statement for the molecule CsI_3 is **[JEE Main 2014]**

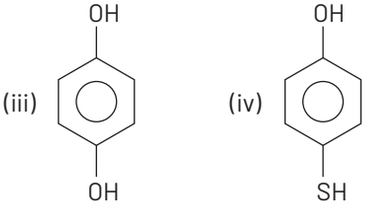
(a) It is a covalent molecule
(b) It contains Cs^+ and I_3^-
(c) It contains Cs^{3+} and I^- ions
(d) It contains Cs^+, I^- and lattice I_2 molecule

Ans. ***(b)***

CsI_3 contains Cs^+ and I_3^- ions.

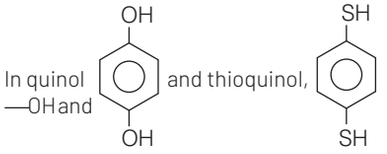
12 For which of the following molecule significant $\mu \neq 0$? **[JEE Main 2014]**



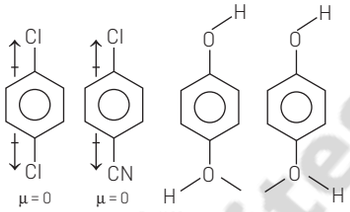


(a) Only (i) (b) (i) and (ii)
(c) Only (iii) (d) (iii) and (iv)

Ans. ***(d)***



—SH groups do not cancel their dipole moments and hence exists as different conformations.



2 different conformers
[$\therefore \mu \neq 0$]
[same as thioquinol]

13 Among the following, the maximum covalent character is shown by the compound **[AIEEE 2011]**

(a) $FeCl_2$ (b) $SnCl_2$
(c) $AlCl_3$ (d) $MgCl_2$

Ans. ***(c)***

Covalent character is favoured by Fajan's rule.
(i) Larger the charge on the ions,
(ii) Smaller the size of cations,
(iii) Larger the size of anions,
(iv) Cation with 18-electron structure (*e.g.*, Cu^+),
then larger the polarising power and the covalent character is favoured.
In all the given compounds, anion is same (Cl^-), hence polarising power is decided by size and charge of cation.
Al^{3+} with maximum charge and smallest size has maximum polarising power hence, $AlCl_3$ is maximum covalent.

14 The number of types of bonds between two carbon atoms in calcium carbide is **[AIEEE 2011]**

(a) one sigma, two pi
(b) one sigma, one pi
(c) two sigma, one pi
(d) two sigma, two pi

Ans. ***(a)***

$$CaC_2 \rightleftharpoons Ca^{2+} + \underset{\text{Carbide ion}}{C_2^{2-}}$$

In carbide ion, two carbon atoms are joined by triple bond (It is isoelectronic with N_2).

$$-C \equiv C-$$

with two π and one σ-bonds.

15 The charge/size ratio of a cation determines its polarising power. Which one of the following sequences represents the increasing order of the polarising power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+} ? **[AIEEE 2007]**

(a) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(b) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(c) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
(d) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$

Ans. ***(c)***

Higher the charge/size ratio, larger is the polarising power.
$\therefore$ $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

16 Lattice energy of an ionic compound depends upon **[AIEEE 2005]**

(a) charge on the ion and size of the ion
(b) packing of ions only
(c) size of the ion only
(d) charge on the ion only

Ans. ***(a)***

Greater the charge and smaller the radius, larger the polarising power and thus, greater the covalent nature. This leads to increase in lattice energy.

17 Which one of the following pairs of molecules will have permanent dipole moments for both members? **[AIEEE 2003]**

(a) SiF_4 and NO_2
(b) NO_2 and CO_2
(c) NO_2 and O_3
(d) SiF_4 and CO_2

Ans. ***(c)***

Both NO_2 and O_3 have angular geometry, thus possess permanent dipole moment. While SiF_4 possesses regular tetrahedral structure and CO_2 possesses a linear structure. In SiF_4 and CO_2, the individual dipoles on the Si—F and O bonds cancel and the molecules have no diple moment.

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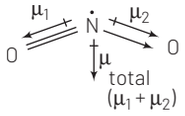
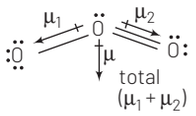
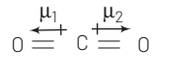


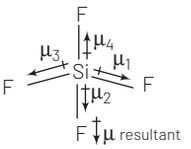
Thus, $\mu_{total} \neq 0$



Thus, $\mu_{total} \neq 0$



$m_{total} = 0 (\mu_1 = -\mu_2)$



$(\mu_1 + \mu_2 + \mu_3 = -\mu_4)$

$\therefore \mu_{total} = 0$

18 Select the correct statement.

[AIEEE 2002]

(a) When a covalent bond is formed, transfer of electrons takes place

(b) Pure H_2O does not contain any ion

(c) A bond is formed when attractive forces overcome repulsive forces

(d) HF is less polar than HBr

Ans. ***(c)***

A bond is formed when attractive forces [$N_A - e_A$ and $N_B - e_B$ or $N_A - e_B$ and $N_B - e_A$] balances the force of repulsion [$e_A - e_B$ or $N_A - N_B$]. Here, N_A and N_B are the nucleus of two atoms, e_A and e_B are the electrons of two atoms.

TOPIC 2
Hybridisation and VSEPR Theory

19 The number of species having non-pyramidal shape among the following is

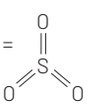
(i) SO_3 (ii) NO_3^-

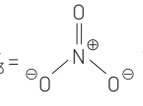
(iii) PCl_3 (iv) CO_3^{2-}

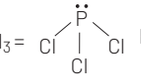
[2021, 27 Aug Shift-II]

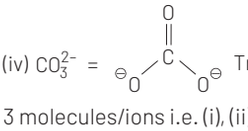
Ans. ***(3)***

The structure of the given compounds are as follows :

(i) SO_3 =  Trigonal planar

(ii) NO_3^- =  Trigonal planar

(iii) PCl_3 =  Pyramidal

(iv) CO_3^{2-} =  Trigonal planar

3 molecules/ions i.e. (i), (ii) and (iv) have non-pyramidal shape.

20 Match List I and List II.

	List I (Species)		**List II** (Hybrid orbitals)
(A)	SF_4	(i)	sp^3d^2
(B)	IF_5	(ii)	d^2sp^3
(C)	NO_2^+	(iii)	sp^3d
(D)	NH_4^+	(iv)	sp^3
		(v)	sp

[2021, 22 July Shift-II]

	A	B	C	D
(a)	(i)	(ii)	(v)	(iii)
(b)	(ii)	(i)	(iv)	(v)
(c)	(iii)	(i)	(v)	(iv)
(d)	(iv)	(iii)	(ii)	(v)

Ans. ***(c)***

A. The S atom in the SF_4 is bonded to 4 fluorine atoms and has 1 lone pair. All of them are in the hybridised orbitals and, there are 5 such orbitals. Due to this, the hybridisation is sp^3d.

B. Since, the central atom iodine has 7 valence electrons out of which 5 electrons form 5 sigma bonds with F atoms and 2 electrons form 1 lone pair making the steric number 6 which implies the hybridisation of the central atom is sp^3d^2.

C. NO_2^+ forms two bonds (double/triple bonds count only once). Therefore, hybridise the ones and one *p*-orbital to give sp^3 hybridisation.

D. The NH_4^+ ion has no pi bonds. As a result, all four electrons contained in the atomic orbitals in the outermost shell of the nitrogen atom can participate in hybridisation, making it sp^3.

The correct matches are :

(A)-(iii), (B)-(i), (C)-(v) and (D)-(iv).

21 The hybridisations of the atomic orbitals of nitrogen in NO_2^-, NO_2^+ and NH_4^+ respectively are

[2021, 20 July Shift-II]

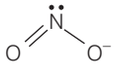
(a) sp^3, sp^2 and sp (b) sp, sp^2 and sp^3

(c) sp^3, sp and sp^2 (d) sp^2, sp and sp^3

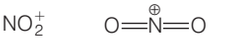
Ans. ***(d)***

Hybridisation = Number of sigma bonds + number of lone pair of electrons + number of coordinate bond.

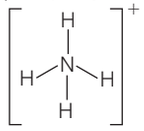
For NO_2^- hybridisation = 2 sigma NO bonds + 1 lone pair on N = 3; so NO_2^- is sp^2-hybridised.

NO_2^- 

For NO_2^+ hybridisation = 2 sigma NO bonds = 2;
so NO_2^+ *sp*-hybridised.

NO_2^+ 

For NO_4^+ Hybridisation = 4 sigma NH bonds = 4; so NH_4^+ is sp^3-hybridised.

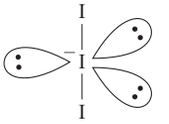
NH_4^+ 

Therefore, hybridisation of N in NO_2^-, NO_2^+, NH_4^+ are sp^2, sp, sp^3 respectively.

22 The number of lone pairs of electron on the central I atom in I_3^- is ..... . **[2021, 20 July Shift-I]**

Ans. ***(3)***

Shape of I_3^- is :



The number of lone pairs of electron on the central atom is 3.

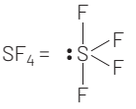
23 The number of species below that have two lone pairs of electrons in their central atom is ..... . (Round off to the nearest integer)

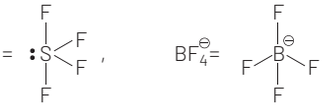
SF_4, BF_4^-, ClF_3, AsF_3, PCl_5, BrF_5, XeF_4, SF_6

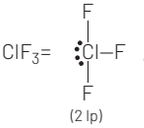
[2021, 18 March Shift-II]

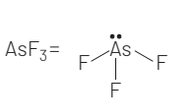
Ans. ***(2)***

Number of lone pairs on central atom in given compounds are as follows

SF_4 =  (1 lp) ,

BF_4^- =  (0 lp)

ClF_3 =  (2 lp) ,

AsF_3 =  (1 lp)

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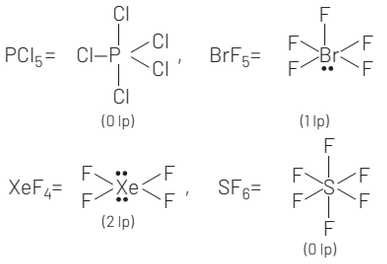


Hence, two (lone pair) lp on central atom is ClF_3 and XeF_4.

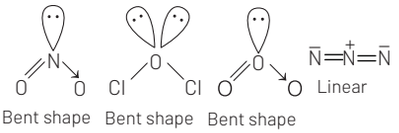
24 Amongst the following, the linear species is

[2021, 17 March Shift-II]

(a) NO_2 (b) Cl_2O
(c) O_3 (d) N_3^-

Ans. ***(d)***

N_3^- is linear species.



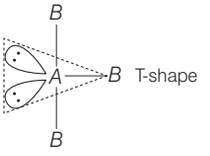
- Hybridisation = Number of sigma bond + number of lone pairs + number of coordinate bonds.
- Hybridisation of N in NO = 1 + 1 + 1 = 3. So, hybridisation is sp^2 and structure is bent or V-shape.
- Hybridisation of O in OCl_2 = 2 + 2 = 4. So, hybridisation is sp^3 and structure is bent or V-shape.
- Hybridisation of O in O_3 = 1 + 1 + 1 = 3. So, hybridisation is sp^2 and structure is bent or V-shape.
- Hybridisation of N in N_3^- = 2. So, hybridisation is *sp* and structure is linear.

25 A central atom in a molecule has two lone pairs of electrons and forms three single bonds. The shape of this molecule is

(a) *see-saw* **[2021, 17 March Shift-I]**
(b) planar triangular
(c) T-shaped
(d) trigonal pyramidal

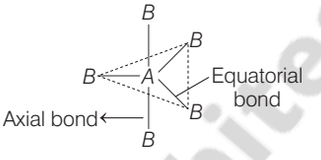
Ans. ***(c)***

2 lone pair + 3 bond pair
Stearic number = 5
So, general formula is AB_3L_2.
(Here, L = number of lone pair.)
Hybridisation = sp^3d.
So, the shape is T- shape.



Note Geometry of the compound having sp^3d hybridisation should to tetragonal bipyramidal (TBP) according to VSEPR theory. But due to two lone pair, geometry is distorted.

In TBP lone pair occupy equatorial position.



26 Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) The H—O—H bond angle in water molecule is 104.5°.

Reason (R) The lone pair - lone pair repulsion of electrons is higher than the bond pair - bond pair repulsion. **[2021, 16 March Shift-I]**

(a) A is false but R is true.
(b) Both A and R are true, but R is not the correct correct explanation of A.
(c) A is true but R is false.
(d) Both A and R are true, and R is the correct explanation of A.

Ans. ***(d)***

Hybridisation of 'O' in H_2O is sp^3 as it is having two lone pair and two sigma bond. Bond angle of sp^3 hybridised compound should be 109.5°.

But in case of water, it is only 104.5° due to repulsion between the lone pairs. Lone pair-lone pair repulsion is higher than bond pair-bond pair repulsion. (VSEPR Theory)

So, both A and R are true and R is the correct explanation of A.

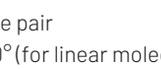
27 The correct shape and I—I—I bond angles respectively in I_3^-, ion are

[2021, 24 Feb Shift-II]

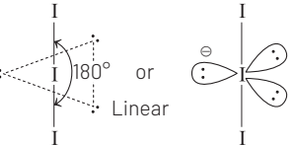
(a) distorted trigonal planar, 135º and 90°
(b) T-shaped, 180° and 90°
(c) Trigonal planar, 120°
(d) Linear, 180°

Ans. ***(d)***

Hybridisation of central I in I_3^- is sp^3d with 3 lone pair and 2 bond pair.

Shape Linear 

Lone pair 3 lone pair
Bond angle 180° (for linear molecule)



28 Which of the following are isostructural pairs ?

A. SO_4^{2-} and CrO_4^{2-}
B. $SiCl_4$ and $TiCl_4$
C. NH_3 and NO_3^-
D. BCl_3 and $BrCl_3$

[2021, 24 Feb Shift-I]

(a) A and B only (b) A and C only
(c) B and C only (d) C and D only

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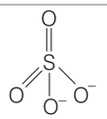
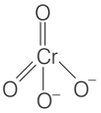
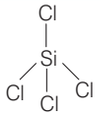
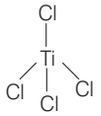
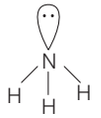
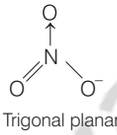
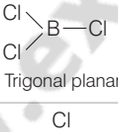
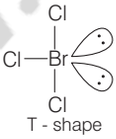
Ans. ***(a)***

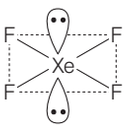
Molecule	H (Steric number)	Hybridisation	B.P.	L.P.	Shape
SO_4^{2-}	4	sp^3	4	0	 Tetrahedral
CrO_4^{2-}	4	sp^3	4	0	 Tetrahedral
$SiCl_4$	4	sp^3	4	0	 Tetrahedral
$TiCl_4$	4	sp^3	4	0	 Tetrahedral
NH_3	4	sp^3	3	1	 Trigonal pyramidal
NO_3^-	4	sp^2	3	0	 Trigonal planar
BCl_3	3	sp^2	3	0	 Trigonal planar
$BrCl_3$	5	sp^3d	3	2	 T - shape

If number of sigma bond (σ), co-ordinate bond and lone pair are same for given pairs, they are isostructural. Hence, SO_4^{2-}, CrO_4^{2-}, $SiCl_4$ and $TiCl_3$ have tetrahedral shape and are isostructural.

29 Which among the following species has unequal bond lengths ? **[2021, 25 Feb Shift-II]**

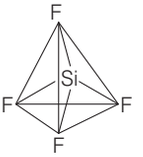
(a) XeF_4 (b) SiF_4
(c) SF_4 (d) BF_4^-

Ans. ***(c)***

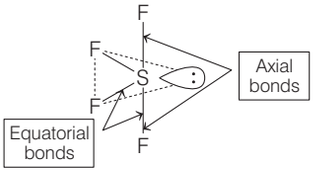
(a) $:\ddot{\underset{\cdot\cdot}{Xe}}F_4$ ⇒ 

Xe (sp^3d^2-hybridised)

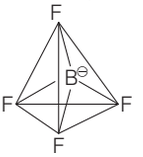
Geometry : Octahedral
Shape : Square planar
It has four equivalent Xe—F bonds in the same plane.

(b) SiF_4 ⇒ 

Si (sp^3-hybridised)
Geometry and shape : Tetrahedral
It has four equivalent Si—F bonds.

(c) $:SF_4$ ⇒ 

S (sp^3d-hybridised)
Geometry : Trigonal bipyramidal
Shape : *see-saw*
Axial S—F bonds are longer than equatorial bonds.

(d) BF_4^- ⇒ 

B (sp^3-hybridised)
Geometry and shape : Tetrahedral
It has four equivalent B—F bonds.
Hence, among given species only SF_4 has unequal bond lengths.

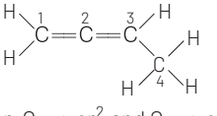
30 In $\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}H_3$ molecule, the hybridisation of carbon 1, 2, 3 and 4 respectively are **[2021, 26 Feb Shift-II]**

(a) sp^3, sp, sp^3, sp^3 (b) sp^2, sp^2, sp^2, sp^3
(c) sp^2, sp, sp^2, sp^3 (d) sp^2, sp^3, sp^2, sp^3

Ans. ***(c)***

$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}H_3$

It is buta -1, 2 - diene,



Here, $C_1 \rightarrow sp^2$, $C_2 \rightarrow sp$, $C_3 \rightarrow sp^2$ and $C_4 \rightarrow sp^3$ hybridised.
So, option (c) is the correct answer.

31 If AB_4 molecule is a polar molecule, a possible geometry of AB_4 is **[2020, 2 Sep Shift-I]**

(a) square pyramidal (b) square planar
(c) rectangular planar (d) tetrahedral

Ans. ***(a)***

If AB_4 molecule is a polar moelcule, a possible geometry of AB_4 is square pyramidal.
All possible structure of AB_4 molecule are as follows :

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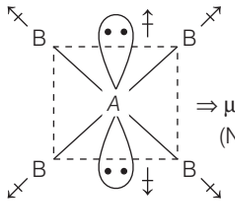
(i) $AB_4 \Rightarrow L = 0 \Rightarrow A$ is sp^3 (tetrahedral) or A is dsp^2 (square planar)
$\Rightarrow$ Dipole moment, $\mu = 0$
(Non-polar)

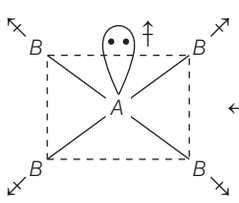
(ii) $AB_4L_2 \Rightarrow L = 2 \Rightarrow A$ is sp^3d^2 (octahedral)
$\Rightarrow \mu = 0$ (Non-polar), because



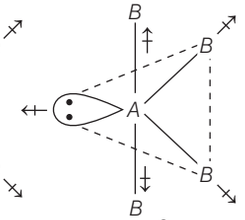
$\Rightarrow \mu_{net} = 0$
(Non-polar)

(Assuming, B is more electronegative than A)

(iii) $AB_4L \Rightarrow L = 1 \Rightarrow A$ is sp^3d (square pyramidal or trigonal bipyramidal)
$\Rightarrow \mu \neq 0$ (polar), because



$\mu_{plane} = 0$
$\mu_{axis} \neq 0$
$\mu_{net} \neq 0$ (polar)
[Square pyramidal]



$\mu_{plane} \neq 0$
$\mu_{axis} \neq 0$
$\mu_{net} \neq 0$ (polar)
[Trigonal pyramidal]

So, it can be seen that when AB_4 molecule is a polar molecule then possible geometry of AB_4 is square pyramidal.

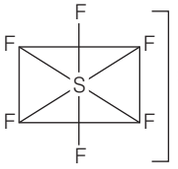
32 The molecular geometry of SF_6 is octahedral. What is the geometry of SF_4 (including lone pair(s) of electrons, if any)? **[2020, 2 Sep Shift-II]**

(a) Tetrahedral (b) Trigonal bipyramidal
(c) Pyramidal (d) Square planar

Ans. ***(b)***

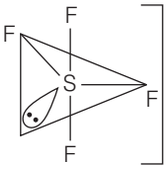
The geometry of SF_6 is octahedral and the geometry of SF_4 is trigonal bipyramidal.

SF_6



S: sp^3d^2-hybridised
Geometry = shape = octahedral

SF_4



S: sp^3d-hybridised
Geometry = trigonal bipyramidal
Shape = *See-saw*

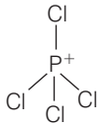
33 The structure of PCl_5 in the solid state is **[2020, 5 Sep Shift-I]**

(a) tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$
(b) trigonal bipyramidal
(c) square planar $[PCl_4]^+$ and octahedral $[PCl_6]^-$
(d) square pyramidal

Ans. ***(a)***

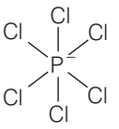
Phosphorus pentachloride (PCl_5) exist as $[PCl_4]^+$ and $[PCl_6]^-$.

Structure of $[PCl_4]^+$



Tetrahedral
(sp^3-hybridisation)

Structure of $[PCl_6]^-$



Octahedral
(sp^2d^2-hybridisation)

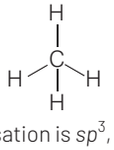
In solid state PCl_5 prefer to exist as oppositely charged ions like $[PCl_4]^+$ and $[PCl_6]^-$ as the ionic bonding enhances the crystalline nature. These structures $[PCl_4]^+$ and $[PCl_6]^-$.

Providing extra stability to solid.

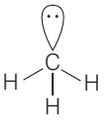
34 The compound that has the largest H—M—H bond angle (M = N, O, S, C) is **[2020, 5 Sep Shift-II]**

(a) H_2O (b) NH_3
(c) H_2S (d) CH_4

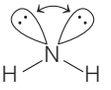
Ans. ***(d)***



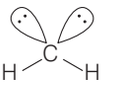
[CH_4 = hybridisation is sp^3, lone pair of electrons is 0, so that bond angle is maximum i.e., = 109°28']



[NH_3= Hybridisation is sp^3, lone pair of electron is one, so that bond angle is 107°]



[H_2O = Hybridisation is sp^3 lone pair of electrons are two, so that bond angle is 104°5′]



[No hybridisation as according to Draga's rule, so that bond angle is 92°]

According to VSEPR theory.

Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair.

35 The ion that has sp^3d^2 hybridisation for the central atom, is **[2019, 8 April Shift-II]**

(a) $[ICl_2]^-$ (b) $[BrF_2]^-$
(c) $[ICl_4]^-$ (d) $[IF_6]^-$

Ans. ***(c)***

Key Idea The hybridisation for a central atom in a species can be calculated using formula

$$H = \frac{1}{2}(V + M - C + A)$$

where,

H = No. of hybridised orbitals used by central atoms.

V = No. of valence electrons of the central atom.

M = No. of mono-valent atoms (bonded).

C = No. of cationic (positive) charge.

A = No. of anionic (negative) charge.

The hybridisation of given species are as follows :

- For $[ICl_2]^-$ and $[BrF_2]^-$
$$H = \frac{1}{2}(7 + 2 - 0 + 1) = 5\,(sp^3d)$$
- For $[ICl_4]^-$,
$$H = \frac{1}{2}(7 + 4 - 0 + 1) = 6\,(sp^3d^2)$$
- For $[IF_6]^-$,
$$H = \frac{1}{2}(7 + 6 - 0 + 1) = 7\,(sp^3d^3)$$

36 The correct statements among I to III are :

I. Valence bond theory cannot explain the color exhibited by transition metal complexes.
II. Valence bond theory can predict quantitatively the magnetic properties of transition metal complexes.
III. Valence bond theory cannot distinguish ligands as weak and strong field ones.

[2019, 9 April Shift-II]

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(a) II and III only (b) I, II and III
(c) I and II only (d) I and III only

Ans. ***(d)***

Among the given statements, correct statements are I and III only. Valence bond theory (VBT) cannot explain the colour exhibited by transition metal complexes. This theory cannot distinguish ligands as weak and strong field ones.

37 The molecule having smallest bond angle is **[AIEEE 2012]**

(a) NCl_3 (b) $AsCl_3$
(c) $SbCl_3$ (d) PCl_3

Ans. ***(c)***

N, P, As, Sb] Group = 15 ; Valence electrons] = 5

MCl_3 has sp^3 hybridized M-element with one lone-pair.

Lone-pair and bond-pair repulsion decreases bond angle. However, the bond-pairs of electrons are much farther away from the central atom than they are in NCl_3. Thus, lone-pair causes even greater distortion in PCl_3, $AsCl_3$ and $SbCl_3$. Thus, bond angle decreases from NCl_3 (maximum) to $SbCl_3$ (minimum).

38 In which of the following pairs, the two species are not isostructural? **[AIEEE 2012]**

(a) CO_3^{2-} and NO_3^-
(b) PCl_4^+ and $SiCl_4$
(c) PF_5 and BrF_5
(d) AlF_6^{3-} and SF_6

Ans. ***(c)***

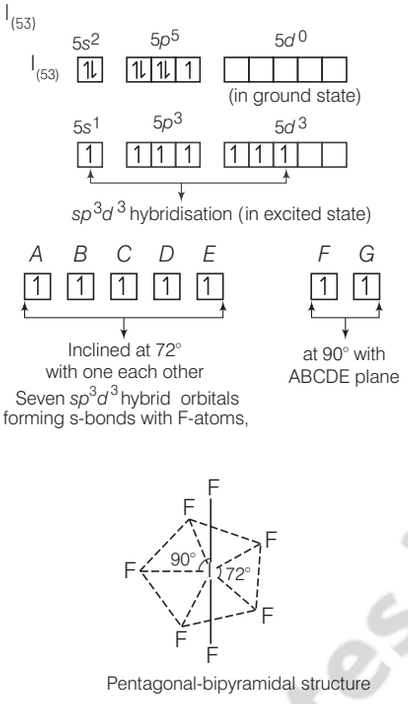
(a) CO_3^{2-}, NO_3^- Triangular planar
(b) PCl_4^+, $SiCl_4$ Tetrahedral
(c) PF_5 Trigonal bipyramidal
BrF_5 Square pyramidal
(d) AlF_6^{3-}, SF_6 Octahedral

39 The structure of IF_7 is **[AIEEE 2011]**

(a) square pyramid
(b) trigonal bipyramid
(c) octahedral
(d) pentagonal bipyramid

Ans. ***(d)***

IF_7 Outer orbital diagram of I



Pentagonal-bipyramidal structure

40 Which of the following has maximum number of lone pairs associated with Xe? **[AIEEE 2011]**

(a) XeO_3 (b) XeF_4
(c) XeF_6 (d) XeF_2

Ans. ***(d)***

	Species	Hybridisation of Xe	Lone pair on Xe	Bonding pairs
(a)	XeO_3	sp^3	1	3
(b)	XeF_4	sp^3d^2	2	4
(c)	XeF_6	sp^3d^3	1	6
(d)	XeF_2	sp^3d	3 (max)	2

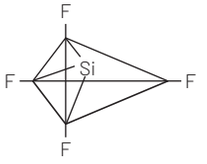
41 In which of the following molecules/ions, all the bonds are not equal? **[AIEEE 2006]**

(a) SF_4 (b) SiF_4
(c) XeF_4 (d) BF_4^-

Ans. ***(a)***

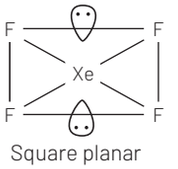
SF_4 has trigonal bipyramidal geometry, lone pair of electrons repels the axial bond pair and decreases the bond angle to 173°.

SiF_4



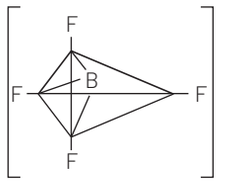
Regular tetrahedral

XeF_4



Square planar

BF_4^-



Tetrahedral

42 The decreasing values of bond angles from NH_3 (107°) to SbH_3 (91°) down group-15 of the periodic table is due to **[AIEEE 2006]**

(a) increasing *bp*-*bp* repulsion
(b) increasing *p*-orbital character in sp^3
(c) decreasing *lp*-*bp* repulsion
(d) decreasing electronegativity

Ans. ***(d)***

$NH_3 > PH_3 > AsH_3 > SbH_3$

As the electronegativity of central atom increases, bonded electron polarise towards central atom more, so repulsion increases and bond angle increases.

43 The molecular shapes of SF_4, CF_4 and XeF_4 are

(a) different with 1, 0 and 2 lone pair of electrons on the central atom, respectively
(b) different with 0, 1 and 2 lone pair of electrons on the central atom, respectively
(c) the same with 1, 1 and 1 lone pair of electrons on the central atom, respectively
(d) the same with 2, 0 and 1 lone pair of electrons on the central atom, respectively **[AIEEE 2005]**

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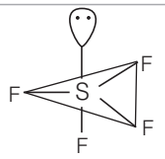
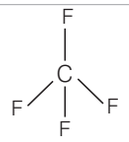
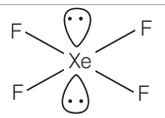
Ans. ***(a)***

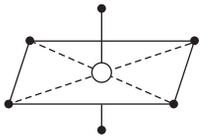
Molecule	Structure	Hybridisation of central atom	Lone pair
SF_4		sp^3d	one
CF_4		sp^3	zero
XeF_4		sp^3d^2	two

44 The maximum number of 90° angles between bond pair-bond pair of electrons is observed in **[AIEEE 2004]**

(a) dsp^3 hybridisation (b) sp^3d hybridisation
(c) dsp^2 hybridisation (d) sp^3d^2 hybridisation

Ans. ***(d)***

sp^3d^2 hybridisation has octahedral structure such that four hybrid orbitals are at 90° *wrt* each other and others two at 90° with first four.



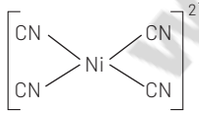
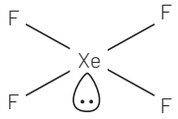
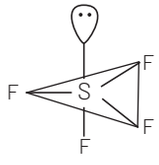
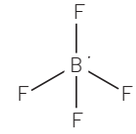
45 Which one of the following has the regular tetrahedral structure ? **[AIEEE 2004]**

(Atomic number : B = 5, S = 16, Ni = 28, Xe = 54)

(a) XeF_4 (b) SF_4 (c) BF_4^- (d) $[Ni(CN)_4]^{2-}$

Ans. ***(c)***

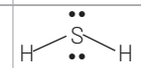
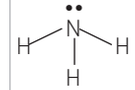
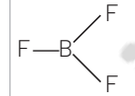
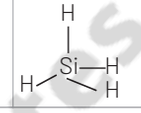
Tetrahedral structure is associated with sp^3 hybridised central atom without any lone pair. *The structure of all the compounds given are as follows*

- $[Ni(CN)_4]^{2-}$  Square planar
- XeF_4  Distorted octahedral
- SF_4  Distorted trigonal bipyramidal
- BF_4^-  Tetrahedral

46 The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is **[AIEEE 2004]**

(a) $H_2S < SiH_4 < NH_3 < BF_3$ (b) $NH_3 < H_2S < SiH_4 < BF_3$
(c) $H_2S < NH_3 < SiH_4 < BF_3$ (d) $H_2S < NH_3 < BF_3 < SiH_4$

Ans. ***(c)***

Species	Structure	*lp*	*bp*	VSEPR	Bond angle
H_2S		2	2	*lp-lp* *lp-bp* *bp-bp*	90°
NH_3		1	3	*lp-bp* *bp→3bp*	107°
BF_3		0	3	*bp-bp*	120°
SiH_4		0	4	*bp-bp*	109° 28′

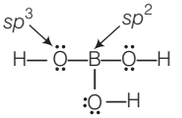
Thus, the order of bond angles is

$H_2S < NH_3 < SiH_4 < BF_3$.

47 The states of hybridisation of boron and oxygen atoms in boric acid (H_3BO_3) are respectively **[AIEEE 2004]**

(a) sp^2 and sp^2 (b) sp^2 and sp^3
(c) sp^3 and sp^2 (d) sp^3 and sp^3

Ans. ***(b)***

H_3BO_3 has structure 

Boron has three bonds, thus sp^2 hybridised. Each oxygen has two bonds and two lone pairs, hence sp^3 hybridised.

48 Which one of the following does not have sp^2 hybridised carbon? **[AIEEE 2004]**

(a) Acetone (b) Acetic acid
(c) Acetonitrile (d) Acetamide

Ans. ***(c)***

(a) $\underset{sp^3}{CH_3}-\underset{sp^2}{\overset{\overset{O}{\|}}{C}}-\underset{sp^3}{CH_3}$ (b) $\underset{sp^3}{CH_3}-\underset{sp^2}{\overset{\overset{O}{\|}}{C}}-OH$

(c) $\underset{sp^3}{CH_3}-\underset{sp}{C}\equiv N$ (d) $\underset{sp^3}{CH_3}-\underset{sp^2}{\overset{\overset{O}{\|}}{C}}-NH_2$

Acetonitrile does not contain sp^2 hybridised carbon.

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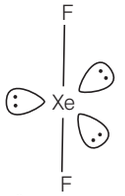
49 The pair of species having identical shapes for molecules of both species, is **[AIEEE 2003]**

(a) CF_4, SF_4 (b) XeF_2, CO_2 (c) BF_3, PCl_3 (d) PF_5, IF_5

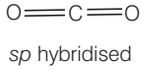
Ans. ***(b)***

XeF_2 contains sp^3d hybridised Xe atom with three lone pairs of electrons. Fluorine atoms occupy axial positions while three lone pairs of elelctrons occupy equitorial positions in trigonal bipyramid.

Since, lone pair of electrons do not considered for the shape of the molecule, thus, shape of XeF_2 comes out to be linear. While C–atom of CO_2 is *sp* hybridised and thus, possesses a linear shape.



sp^3d hybridised Xe-atom



sp hybridised C-atom

50 Which one of the following compounds has the smallest bond angle? **[AIEEE 2003]**

(a) SO_2 (b) OH_2 (c) SH_2 (d) NH_3

Ans. ***(c)***

Molecule	Hybridisation	Repulsion	Bond angle
SO_2	sp^2	$\frac{lp-bp, bp-bp}{lp-lp, bp-lp}$	119.5°
OH_2	sp^3	$\underline{bp-bp}$	104.5°
SH_2	sp^3	–do–	90°
NH_3	sp^3	$lp-bp, bp-bp$	107°

51 Bond angle of 109°28′ is found in **[AIEEE 2002]**

(a) NH_3 (b) H_2O (c) $\overset{\oplus}{C}H_5$ (d) $\overset{\oplus}{N}H_4$

Ans. ***(d)***

109° 28′, it means pure regular tetrahedral geometry.

(a) NH_3, sp^3, pyramidal (b) H_2O, sp^3, bent

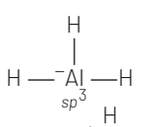
(c) CH_5^+, does not exist (d) NH_4^+, sp^3, tetrahedral

52 Hybridisation of the underline atom changes in **[AIEEE 2002]**

(a) $\underline{Al}H_3$ changes to AlH_4^- (b) $H_2\underline{O}$ changes to H_3O^+

(c) $\underline{N}H_3$ changes to NH_4^+ (d) In all cases

Ans. ***(a)***

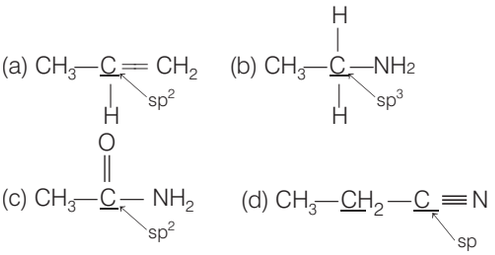
(a)	AlH_3 sp^2	 sp^3	Change in hybridisation as well as in shape
(b)	H_2O sp^3 (2 *bp* +2 *lp*)	H_3O^+ sp^3 (3*bp* + 1 *lp*)	Change in shape only, bent to pyramidal
(c)	NH_3 sp^3 (3 *bp* + 1 *lp*)	NH_4^+ sp^3 (4 *bp*)	Change in shape only, pyramidal to tetrahedral

53 Underlined carbon is sp^3 hybridised in **[AIEEE 2002]**

(a) $CH_3\underline{C}H = CH_2$ (b) $CH_3\underline{C}H_2NH_2$

(c) $CH_3\underline{C}ONH_2$ (d) $CH_3CH_2\underline{C}N$

Ans. ***(b)***



54 The number of lone pairs on Xe in XeF_2, XeF_4 and XeF_6 respectively, are **[AIEEE 2002]**

(a) 3, 2, 1 (b) 2, 4, 6 (c) 1, 2, 3 (d) 6, 4, 2

Ans. ***(a)***

Number of lone pairs

= (Total number of electron pairs) – (Number of shared pairs)

Number of electron pairs

$= \frac{1}{2}$[Number of valence electrons of central atom + Number of atoms linked to central aom]

For XeF_2

Number of e^- pairs $= \frac{1}{2}[8+2] = 5$

Number of lone pairs $= 5-2 = 3$

For XeF_4, Number of e^- pairs $= \frac{1}{2}[8+4] = 6$

Number of lone pairs $= 6-4 = 2$

For XeF_6,

Number of e^- pairs $= \frac{1}{2}[8+6] = 7$

Number of lone pairs $= 7-6 = 1$

Thus, number of lone pairs of electrons in XeF_2, XeF_4 and XeF_6 are 3, 2, 1 respectively.

TOPIC 3

Molecular Orbital Theory, Hydrogen and Metallic Bonding

55 The spin-only magnetic moment value of B_2^+ species is ..... $\times 10^{-2}$ BM. (Nearest integer) [Given, $\sqrt{3} = 1.73$] **[2021, 1 Sep Shift-II]**

Ans. ***(173)***

Spin only mangnetic moment is given as

$$\mu_S = \sqrt{n(n+2)}\ \text{BM}$$

where, n = number of unpaired electrons

Electronic configuration of B_2^+ is as follows

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$B_2^+ = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^1 \approx \pi 2p_z^0$

$\therefore B_2^+$ has one unpaired electron,

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM} = 173 \times 10^{-2} \text{ BM}$$

$\therefore \quad x \times 10^{-2} = 173 \times 10^{-2} \therefore x = 173$

Hence, answer is 173.

56 According to molecular orbital theory, the number of unpaired electron(s) in O_2^{2-} is ..... . **[2021, 31 Aug Shift-II]**

Ans. ***(0)***

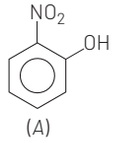
In O_2^{2-}, 18 electrons are present.

Configuration is given by

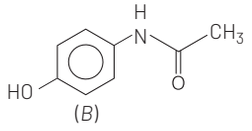
$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2$$
$$\pi^* 2p_x^2 = \pi^* 2p_y^2, \sigma^* 2p_z^0$$

So, number of unpaired electrons in $O_2^{2-} = 0$.

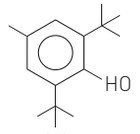
57 The compound/s which will show significant intermolecular H-bonding is/are



(A)



(B)



(C)

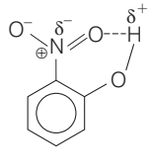
[2021, 27 Aug Shift-II]

(a) (B) only (b) (C) only

(c) (A) and (B) (d) (A), (B) and (C)

Ans. ***(a)***

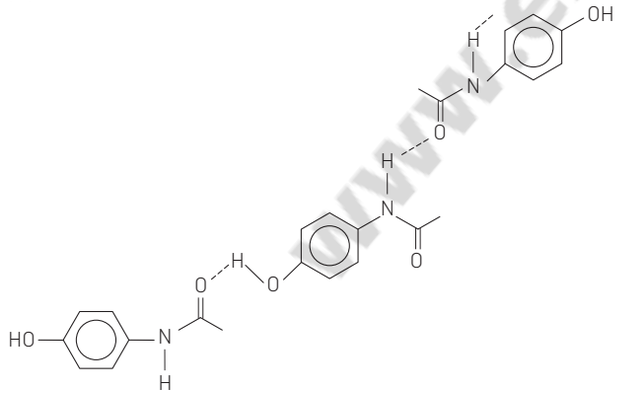
(A)



(Hydrogen bonding)

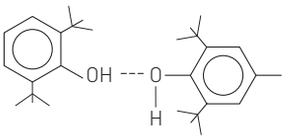
In *o*-nitrophenol intramolecular hydrogen bonding takes place.

(B)



Extensive H-bonding is observed in this case as two H-atoms bonded to strongly electronegative atoms (nitrogen, oxygen) are present. H-bonding occurs when H-bonded to strongly electronegative atoms exists in the vicinity of other electronegative atoms possessing lone pairs of electron.

(C)



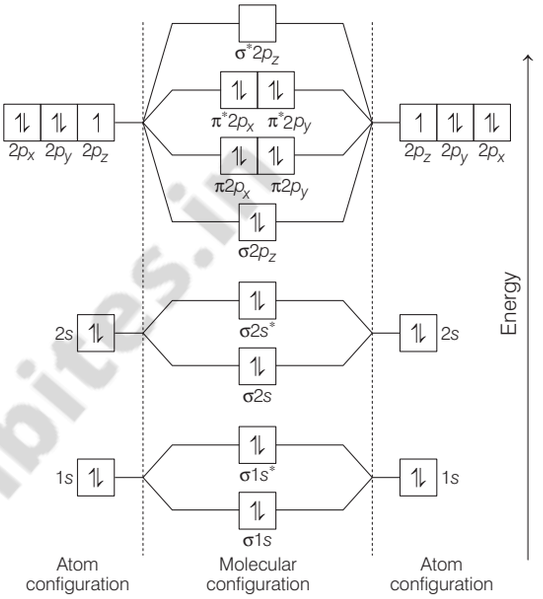
Here, only one hydrogen atom bonded to electronegative oxygen atom is present. So, intermolecular H-bonding is present but not so extensive.

So, option (a) is correct.

58 The total number of electrons in all bonding molecular orbitals of O_2^{2-} is ..... .

(Round off to the nearest integer) **[2021, 27 July Shift-II]**

Ans. ***(10)***



Configuration $(O_2^{2-}) = \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < (\pi 2p_x = \pi 2p_z)^4 (\pi^* 2p_x = \pi^* 2p_y)^2$

Number of electrons in all bonding molecular orbitals = 10

Number of electrons in all anti-bonding molecular orbitals = 8

59 The difference between bond orders of CO and $NO^{\oplus}$ is $x/2$. where, $x =$ ..... .

(Round off to the nearest integer). **[2021, 27 July Shift-I]**

Ans. ***(0)***

Electronic configuration of CO (14 electrons).

$(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2, \sigma 2p_z^2$

$$\text{Bond order} = \frac{[\text{No. of bonding electron} - \text{No. of antibonding electron}]}{2}$$

$$= \frac{10-4}{2} = 3$$

Electronic configuration of NO^+ (14 electrons)

$(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$

$$\text{BO} = \frac{10-4}{2} = 3$$

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Bond order of both CO and $NO^{\oplus} = 3$

Difference $= 0 = \frac{x}{2}$; $x = 0$

60 The bond order and magnetic behaviour of O_2^- ion are, respectively **[2021, 26 Aug Shift-II]**

(a) 1.5 and paramagnetic
(b) 1.5 and diamagnetic
(c) 2 and diamagnetic
(d) 1 and paramagnetic

Ans. ***(a)***

O_2^- (Total electrons = 17)

$= \sigma 1s^2, \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2, \pi 2p_x^2$

$= \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1, \sigma^* 2p_z^0$

Number of unpaired electron = 1

So, it is paramagnetic.

$$\text{Bond order} = \frac{n_b - n_a}{2}$$

$$= \frac{10-7}{2} = 1.5$$

61 In the following the correct bond order sequence is **[2021, 25 July Shift-II]**

(a) $O_2^{2-} > O_2^+ > O_2^- > O_2$
(b) $O_2^+ > O_2^- > O_2^{2-} > O_2$
(c) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
(d) $O_2 > O_2^- > O_2^{2-} > O_2^+$

Ans. ***(c)***

$$\text{Bond order} = \frac{\left(\begin{matrix}\text{No. of electrons in}\\ \text{bonding M.O.}\end{matrix}\right) - \left(\begin{matrix}\text{No. of electrons in}\\ \text{anti-bonding M.O.}\end{matrix}\right)}{2}$$

Here, antibonding molecular orbital electrons denoted by (*).

- $O_2^+ = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2$
  $(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^1 = \pi^* 2p_y)$
  $\text{B.O.} = \frac{1}{2}(10-5) = 2.5$
- $O_2 = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2$
  $(\pi 2p_z^2 = \pi^* 2p_y^2)(\pi^* 2p_x^1 = \pi^* 2p_y^1)$
  $\text{B.O.} = \frac{1}{2}(10-6) = 2$
- $O_2^- = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2$
  $(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^2 = \pi^* 2p_y^1)$
  $\text{B.O.} = \frac{1}{2}(10-7) = 1.5$
- $O_2^{2-} = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2$
  $(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^2 = \pi^* 2p_y^2)$
  $\text{B.O.} = \frac{1}{2}(10-8) = 1$

$\therefore$ Correct order of bond order

$= O_2^+ > O_2 > O_2^- > O_2^{2-}$

62 Match List-I with List-II

	List-I (Molecule)		List-II (Bond order)
A.	Ne_2	(i)	1
B.	N_2	(ii)	2
C.	F_2	(iii)	0
D.	O_2	(iv)	3

Choose the correct answer from the options given below. **[2021, 26 Feb Shift-II]**

	A	B	C	D		A	B	C	D
(a)	(iii)	(iv)	(i)	(ii)	(b)	(i)	(ii)	(iii)	(iv)
(c)	(ii)	(i)	(iv)	(iii)	(d)	(iv)	(iii)	(ii)	(i)

Ans. ***(a)***

(A) Ne_2 $(20e^-)$

$\Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^2\ \pi^* 2p_y^2\ \sigma^* 2p_z^2$

$$\text{Bond order} = \frac{10-10}{2} = 0$$

$\Rightarrow$ (iii) of List-II.

(B) N_2 $(14e^-)$

$\Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2\ \pi 2p_x^2, \pi 2p_y^2 \sigma 2p_z^2$

$$\text{Bond order} = \frac{10-4}{2} = 3 \Rightarrow \text{(iv) of List-II.}$$

(c) F_2 $(18e^-)$

$\Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_y^2\ \pi^* 2p_y^2$

$$\text{Bond order} = \frac{10-8}{2} = 1 \Rightarrow \text{(i) of List-II.}$$

(d) O_2 $(16e^-)$

$\Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1\ \pi^* 2p_y^1$

$$\text{Bond order} = \frac{10-6}{2} = 2 \Rightarrow \text{(ii) of List-II.}$$

The correct matching is option (a).

Note : Bond order

$$= \frac{-\text{No. of electrons in bonding MO}}{2}$$

No. of electrons in antibonding MO (Molecular Orbital)

63 According to molecular orbital theory, the species among the following that does not exist is **[2021, 25 Feb Shift-I]**

(a) O_2^{2-} (b) He_2^- (c) Be_2 (d) He_2^+

Ans. ***(c)***

According to Molecular Orbital Theory (MOT), electronic configuration and their bond order of given options are as follows

- $O_2^{2-} = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^2, \pi^* 2p_y^2$

  $$\text{Bond order} = \frac{[\text{No. of bonding electrons} - \text{No. of antibonding electrons}]}{2}$$

  $$= \frac{10-8}{2} = \frac{2}{2} = 1$$
- $He_2^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^1$

  $$\text{Bond order} = \frac{3-2}{2} = \frac{1}{2} = 0.5$$
- $Be_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$

  $$\text{Bond order} = \frac{4-4}{2} = 0$$
- $He_2^+ = \sigma 1s^2, \sigma^* 1s^1$

  $$\text{Bond order} = \frac{2-1}{2} = \frac{1}{2} = 0.5$$

If bond order of chemical species is zero then that chemical species does not exist.

Therefore, Be_2 does not exist.

64 A hard substance melts at high temperature and is an insulator in both solid and in molten state. This solid is most likely to be a/an **[2021, 18 March Shift-II]**

(a) ionic solid (b) molecular solid
(c) metallic solid (d) covalent solid

Ans. ***(d)***

Covalent or network solid have very high melting point and they are insulators in their solid and molten form.

If a substance is an insulator in both solid and molten phases, then it cannot be ionic or metallic solid. If the melting point is higher, then it cannot be a molecular solid.

$\therefore$ It should be covalent network solid.

65 Of the species, NO, NO^+, NO^{2+} and NO^-, the one with minimum bond strength is **[2020, 5 Sep Shift-I]**

(a) NO^+ (b) NO (c) NO^{2+} (d) NO^-

Ans. ***(d)***

Energy order of MOs

$$\text{B.O.} = \frac{N_b - N_a}{2}$$

$\sigma_{1s} \sigma^*_{1s} \sigma_{2s} \sigma^*_{2s} \pi_{2p_x} = \pi_{2p_y} \sigma_{2p_z} \pi^*_{2p_x} = \pi^*_{2p_y}$

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$NO(15e^-)$: 2 2 2 2 2 2 2 1 $0 \rightarrow \frac{10-5}{2} = 2.5$

$N\overset{+}{O}(14e^-)$: 2 2 2 2 2 2 2 0 $0 \rightarrow \frac{10-4}{2} = 3$

$N\overset{2+}{O}(13e^-)$: 2 2 2 2 2 2 1 0 $0 \rightarrow \frac{9-4}{2} = 2.5$

$N\bar{O}(16e^-)$: 2 2 2 2 2 2 2 1 $1 \rightarrow \frac{10-6}{2} = 2$

We know,

$$\text{Bond length} \propto \frac{1}{\text{BO (Bond order)}}$$

$$\propto \frac{1}{\text{Bond strength}}$$

So, the order of bond strength :

$$NO^+ > NO = NO^{2+} > NO^-$$

So, NO^- has minimum bond strength.

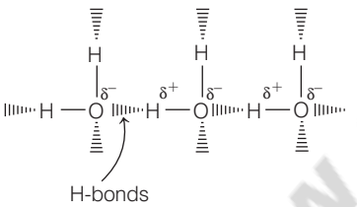
66 If the boiling point of H_2O is 373 K, the boiling point of H_2S will be **[2020, 3 Sep Shift-I]**

(a) less than 300 K
(b) equal to 373 K
(c) more than 373 K
(d) greater than 300 K but less than 373 K

Ans. ***(a)***

Two O—H bonds of a H_2O molecule make stronger and extensive intermolecular hydrogen bonds which lead two association of H_2O molecules into water or $H_2O(l)$. One H_2O molecule can make four H-bonds.

$$nH_2O \xrightarrow[\text{intermolecular H—bonds}]{\text{Association through}} \underbrace{(H_2O)_n \text{ or } H_2O(l)}_{\text{Water}}$$



But S—H bonds of H_2S cannot make H-bonds. So, H_2S is a gas at room temperature but H_2O is a liquid (water). So, boiling point of H_2O is more 373 K than H_2S, because :

Boiling point ∝ molecular association.

67 The bond order and the magnetic characteristics of CN^- are **[2020, 7 Jan Shift-II]**

(a) 3, diamagnetic
(b) $2\frac{1}{2}$, paramagnetic
(c) 3, paramagnetic
(d) $2\frac{1}{2}$, diamagnetic

Ans. ***(a)***

CN^- has 14 electrons (6 from C, 7 from N and 1 for negative charge).

Its MO configuration must be similar to

$$N_2 : \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^2$$

$$\therefore \quad \text{Bond order} = \frac{10-4}{2} = 3$$

As there is no unpaired electron in CN^-, thus it is diamagnetic.

68 If the magnetic moment of a dioxygen species is 1.73 B.M, it may be. **[2020, 9 Jan Shift-II]**

(a) O_2, O_2^- or O_2^+ (b) O_2^- or O_2^+ (c) O_2 or O_2^- (d) O_2 or O_2^+

Ans. ***(a)***

	Species and number of electrons	Molecular orbital electronic configuration	Number of unpaired electrons (n) and magnetic moment
1.	O_2-16 electrons	$\sigma 1s$ $\sigma^* 1s$ $\sigma 2s$ $\sigma^* 2s$ $\sigma 2p_z$ ⇅ ⇅ ⇅ ⇅ ⇅ $\pi 2p_X = \pi 2p_Y$ $\pi 2p_X^* = \pi 2p_Y^*$ $\sigma^* 2p_Z$ ⇅ ⇅ 1 1	$n = 2, \mu = \sqrt{n(n+2)}$ $\mu = \sqrt{2\times 4}$ BM $= 2.82$ BM
2.	O_2^+-15 electrons	⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ 1	$n = 1,\ \mu = \sqrt{1\times 3}$ $= 1.73$ BM
3.	O_2^--17 electrons	⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ 1	$n = 1, \mu = 1.73$ BM

69 Among the following molecules/ions,

$$C_2^{2-}, N_2^{2-}, O_2^{2-}, O_2$$

Which one is diamagnetic and has the shortest bond length? **[2019, 8 April Shift-II]**

(a) C_2^{2-} (b) O_2 (c) O_2^{2-} (d) N_2^{2-}

Ans. ***(a)***

Species	MO energy order	Bond order (BO)	n, no. of unpaired e^-	Magnetic character
$C_2^{2-}(14e^-)$	$[8\bar{e}]\pi_{2p_x^2} = \pi_{2p_y^2}\sigma_{2p_z^2}$	$\frac{6-0}{2} = 3$	0	Diamagnetic
$O_2(16e^-)$	$[8\bar{e}]\sigma_{2p_z^2}\pi_{2p_x^2} = \pi_{2p_y^2}\overset{*}{\pi}_{2p_x^1} = \overset{*}{\pi}_{2p_y^1}$	$\frac{6-2}{2} = 2$	2	Paramagnetic
$O_2^{2-}(18e^-)$	$[8\bar{e}]\sigma_{2p_z^2}\pi_{2p_x^2} = \pi_{2p_y^2}\overset{*}{\pi}_{2p_x^2} = \overset{*}{\pi}_{2p_y^2}$	$\frac{6-4}{2} = 1$	0	Diamagnetic
$N_2^{2-}(16e^-)$	$[8\bar{e}]\pi_{2p_x^2} = \pi_{2p_y^2}\sigma_{2p_z^2}\overset{*}{\pi}_{2p_x^1} = \overset{*}{\pi}_{2p_y^1}$	$\frac{6-2}{2} = 2$	2	Paramagnetic

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$$\text{Bond length} \propto \frac{1}{\text{BO (Bond order)}}$$

So order of bond length

$$\underset{(BO=3)}{C_2^2} < \underset{(BO=2)}{O_2} = \underset{}{N_2^{2-}} < \underset{(BO=1)}{O_2^{2-}}$$

The diamagnetic species with shortest bond length is C_2^{2-} (option-a).

70 Among the following, the molecule expected to be stabilised by anion formation is C_2, O_2, NO, F_2.

[2019, 9 April Shift-I]

(a) C_2 (b) F_2
(c) NO (d) O_2

Ans. ***(a)***

C_2 will be stabilised after forming anion. The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. There are twelve electrons in C_2. After forming anion (i.e. C_2^-), the electronic configuration is

- $C_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2\ (\sigma 2s)^2$ $(\sigma^* 2s)^2\ (\pi 2p_x^2 = \pi 2p_y^2)(\sigma 2p_z^1)$ or $KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2).\sigma 2p_z^1$

  $$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(9-4) = 2.5$$

For other options such as F_2^-, O_2^-, NO^-, the electronic configurations are as follows :

- $F_2^- : (\sigma 1s)^2\ (\sigma^* 1s)^2 (\sigma 2s)^2$ $(\sigma^* 2s)^2 (\sigma 2p_z)^2$ $(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^2 = \pi^* 2p_y^2)(\sigma^* 2p_z^1)$

  Bond order $= 1/2(N_b - N_a) = 1/2(10-9) = 0.5$

- $O_2^- : (\sigma 1s)^{2\cdot} (\sigma^* 1s)^2\ (\sigma 2s)^2$ $(\sigma^* 2s)^2\ (\sigma 2p_z)^2$ $(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^2 = \pi^* 2p_y^1)$

  $$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-7) = 1.5$$

- $NO^- : (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2$ $(\sigma^* 2s)^2 (\sigma 2p_z)^2$ $(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^1 = \pi^* 2p_y^1)$

  $$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-6) = 2$$

The value of bond order of C_2^- is highest among the given options. Bond order between two atoms in a molecule may be taken as an approximate measure of the bond length.

The bond length decreases as bond order increases. As a result, stability of a molecule increases.

71 Among the following species, the diamagnetic molecule is

[2019, 9 April Shift-II]

(a) CO (b) B_2
(c) NO (d) O_2

Ans. ***(a)***

Key Idea Magnetic nature can be detected by molecular orbital theory. Presence of unpaired electrons means paramagnetic and absence of unpaired electrons means diamagnetic in nature.

Among the given options, CO is a diamagnetic molecule. It can be proved by molecular orbital (MO) theory. The electronic configuration of given diatomic molecules are given below.

- CO (Number of electrons = 14)

  Electronic configuration $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$ $\sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2$

  Since, there is no unpaired electron in the CO molecule, so it is diamagnetic.

- NO (Number of electrons = 15)

  Electronic configuration $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2,$ $\sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2,$ $\pi^* 2p_x^1 \approx \pi^* 2p_y^0$

  Since, NO has one unpaired electron in $\pi^* 2p_x^1$ orbital, so it is paramagnetic.

- B_2 (Number of electrons = 10)

  Electronic configuration $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$ $\pi 2p_x^1 \approx \pi p_y^1$

  Since, two unpaired electrons are present in $\pi 2p_x^1$ and $\pi 2p_y^1$ orbital. So, it is paramagnetic.

- O_2 (Number of electrons = 16)

  Electronic configuration $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2,$ $\sigma^* 2s^2, \sigma 2pz^2, \pi 2p_x^2 \approx \pi 2p_y^2,$ $\pi^* 2p_x^1 \approx \pi^* 2p_y^1$

  Since, two unpaired electrons are present in $\pi^* 2p_x^1$ and $\pi^* 2p_y^1$ orbital. So, it is also paramagnetic.

72 During the change of O_2 to O_2^-, the incoming electron goes to the orbital. **[2019, 10 April Shift-I]**

(a) $\pi 2p_x$ (b) $\pi^* 2p_x$
(c) $\pi 2p_y$ (d) $\sigma^* 2p_z$

Ans. ***(b)***

The change of O_2 to O_2^- can be as follows:

$$\underset{\text{[Dioxygen]}}{O_2\,(16\,e^-)} \xrightarrow{+e^-} \underset{\text{[Super-oxide]}}{O_2^-\,(17\,e^-)}$$
$$\rightarrow \text{Energy} \qquad\qquad \rightarrow \text{Energy}$$

$[8e^-]\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \overset{*}{\pi} 2p_x^1 = \overset{*}{\pi} 2p_y^1$ (Half-filled anti-bonding π^*-MO_s)

$[8e^-]\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \overset{*}{\pi} 2p_x^2 = \overset{*}{\pi} 2p_y^1$

So, in the formation of O_2^- from O_2, the 17th electron goes to the $\overset{*}{\pi} 2p_x$ or $\overset{*}{\pi} 2p_y$ molecular orbital (anti-bonding) which is half-filled in O_2.

73 According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^-?

[2019, 9 Jan Shift-I]

(a) Both are unstable
(b) Li_2^+ is unstable and Li_2^- is stable
(c) Both are stable
(d) Li_2^+ is stable and Li_2^- is unstable

Ans. ***(d)***

Considering molecular orbital theory (MOT) :

The electronic configuration of

$$Li_2^+ (Z = 5) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^1$$

$$\text{Bond order (BO)} = \frac{N_b - N_a}{2} = \frac{3-2}{2} = \frac{1}{2}$$

The electronic configuration of

$$Li_2^- (Z = 7) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^1$$

$$\text{Bond order (BO)} = \frac{N_b - N_a}{2} = \frac{4-3}{2} = \frac{1}{2}$$

For the species having the same value of BO, the specie having lesser number of antibonding electrons [N_a] will be more stable.

Here, N_a of Li_2^+ (2) < N_a of Li_2^- (3).

So, their order of stability will be $Li_2^+ > Li_2^-$.

74 In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic? **[2019, 9 Jan Shift-II]**

(a) $O_2 \rightarrow O_2^+$
(b) $N_2 \rightarrow N_2^+$
(c) $O_2 \rightarrow O_2^{2-}$
(d) $NO \rightarrow NO^+$

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Ans. ***(d)***

Species	Valence MOs	Bond Order $\left(\frac{N_b - N_a}{2}\right)$	Magnetic Nature
$NO(15e^-)$	$[8e^-]\ \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$ $\pi^* 2p_x^1 = \pi^* 2p_y^0 \sigma^* 2pz^0$	$\frac{6-1}{2} = 2.5$	Paramagnetic
$-e^-$			
$NO^+(14e^-)$	$[8e^-]\ \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$ $\pi^* 2p_x^0 = \pi^* 2p_y^0 \sigma^* 2p_z^0$	$\frac{6-0}{2} = 3$	Diamagnetic
$N_2(14e^-)$	$[8e^-] \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$	$\frac{6-0}{2} = 3$	Diamagnetic
$-e^-$			
$N_2^+(13e^-)$	$\pi^* 2p_x^0 = \pi^* 2p_y^0, \sigma 2p_z^0$ $[8e^-] \pi 2p_x^2 = \pi 2p_y^2 \sigma\ 2p_{z^1}$ $\pi^* 2p_x^0 = \pi^* 2p_y^0 \sigma^* 2pz_0$	$\frac{5-0}{2} = 2.5$	Paramagnetic
$O_2(16e^-)$	$[8e^-]\ \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi^* 2p_x^1 = \pi^* 2p_y^1 \sigma^* 2p_z^0$	$\frac{6-2}{2} = 2$	Paramagnetic
$-e^-$			
$O_2^+(15e^-)$	$[8e^-]\ \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi^* 2p_x^1 = \pi^* 2p_y^0 \sigma^* 2p_z^0$	$\frac{6-1}{2} = 2.5$	Paramagnetic
$+2e^-$			
$O_2^{2-}(18e^-)$	$[8e^-]\ \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi^* 2p_x^2 = \pi^* 2p_y^2 \sigma^* 2p_z^0$	$\frac{6-4}{2} = 1$	Diamagnetic

So, only in the conversion of $NO \rightarrow NO^+$, the bond order has increased $(2.5 \rightarrow 3)$ and paramagnetic character has changed to diamagnetic.

75 Two pi and half sigma bonds are present in **[2019, 10 Jan Shift-I]**

(a) O_2^+ (b) N_2
(c) N_2^+ (d) O_2

Ans. ***(c)***

The energy order of MOs of the given species are as follows:

$O_2(16\,e^-\text{'s}) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1,$

$O_2^+(15e^-\text{'s}) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^0$

$N_2(14e^-\text{'s}) = \sigma 1s^2\ \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$

$N_2^+(13e^-\text{'s}) = \sigma 1s^2 \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_z^2 \sigma 2p_z^1$

Thus, in case of N_2^+, two π-bonds and half σ-bond are present in the bonding MOs.

76 According to molecular orbital theory, which of the following will not be a viable molecule? **[JEE Main 2018]**

(a) He_2^{2+} (b) He_2^+ (c) H_2^- (d) H_2^{2-}

Ans. ***(d)***

Key Idea According to M.O.T, the viability of any molecule can be judged through the calculation of bond order.

Electronic	Configuration	Bond order
He_2^+	$\sigma_{1s^2} \sigma^*_{1s^1}$	$\frac{2-1}{2} = 0.5$
H_2^-	$\sigma_{1s^2} \sigma^*_{1s^1}$	$\frac{2-1}{2} = 0.5$
H_2^{2-}	$\sigma_{1s^2} \sigma^*_{1s^2}$	$\frac{2-2}{2} = 0$
He_2^{2+}	σ_{1s^2}	$\frac{2-0}{2} = 1$

The molecule having zero bond order will not be viable hence, H_2^{2-} (option d) is the correct answer.

77 Which of the following species is not paramagnetic? **[JEE Main 2017]**

(a) NO (b) CO (c) O_2 (d) B_2

Ans. ***(b)***

To identify the magnetic nature we need to check the molecular orbital configuration. If all orbitals are fully occupied, species is diamagnetic while when one or more molecular orbitals is/are singly occupied, species is paramagnetic.

(a) $NO(7 + 8 = 15) - \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \pi 2p_z^2, \pi^* 2p_x^1 = \pi^* 2p_y^0$
One unpaired electron is present.
Hence, it is paramagnetic.

(b) $CO(6 + 8 = 14) - \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$
No unpaired electron is present.
Hence, it is diamagnetic.

(c) $O_2(8 + 8 = 16) - \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_x^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$
Two unpaired electrons are present.
Hence, it is paramagnetic.

(d) $B_2(5 + 5) - \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 = \pi 2p_y^1$
Two unpaired electrons are present.
Hence, it is paramagnetic.

78 Which one of the following molecules is expected to exhibit diamagnetic behaviour? **[JEE Main 2013]**

(a) C_2 (b) N_2 (c) O_2 (d) S_2

Ans. ***(a, b)***

$C_2(6 + 6 = 12) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$

Since, all the electrons are paired, it is a diamagnetic specie.

$N_2\ (7 + 7 = 14) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2,\ \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

It is also a diamagnetic specie because of the absence of unpaired electrons.

$O_2\ (8 + 8 = 16)$
or $S_2 = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2\ , \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$

Since, O_2 or S_2 contain 2 unpaired electrons, therefore they are paramagnetic.

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79 In which of the following pairs of molecules/ions both the species are not likely to exist? **[JEE Main 2013]**

(a) H_2^+, He_2^{2-} (b) H_2^-, He_2^{2-}
(c) H_2^{2+}, He_2 (d) H_2^-, He_2^{2+}

Ans. ***(c)***

Species having zero or negative bond order do not exist.

$H_2^{2+}(1+1-2=0) = \sigma 1s^0$

Bond order = 0

$He_2\ (2+2=4) = \sigma 1s^2, \overset{*}{\sigma} 1s^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$$

So, both H_2^{2+} and He_2 do not exist.

80 Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of **[JEE Main 2013]**

(a) $Li_2 < Li_2^+ < Li_2^-$
(b) $Li_2^- < Li_2^+ < Li_2$
(c) $Li_2 < Li_2^- < Li_2^+$
(d) $Li_2^- < Li_2 < Li_2^+$

Ans. ***(b)***

$Li_2\ (3+3=6) = \sigma 1s^2,\ \overset{*}{\sigma} 1s^2, \sigma 2s^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4-2}{2} = 1$$

$Li_2^+\ (3+3-1=5) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^1$

$$\text{Bond order} = \frac{3-2}{2} = \frac{1}{2} = 0.5$$

$Li_2^-\ (3+3+1=7)$

$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^1$

$$\text{Bond order} = \frac{4-3}{2} = \frac{1}{2} = 0.5$$

Stability order is $Li_2 > Li_2^+ > Li_2^-$ (because Li_2^- have more number of electrons in antibonding orbitals which destabilises the species).

81 Using MO theory, predict which of the following species has the shortest bond length? **[AIEEE 2009]**

(a) O_2^{2+} (b) O_2^+
(c) O_2^- (d) O_2^{2-}

Ans. ***(a)***

Higher the bond order, shorter is the bond length O_2^{2+} has the shortest bond length (BO = 3)

Bond order of remaining species are

O_2^+ (2.5), O_2^- (1.5) and O_2^{2-} (1)

82 Which one of the following constitutes a group of the isoelectronic species? **[AIEEE 2008]**

(a) C_2^{2-}, O_2^-, CO, NO
(b) NO^+, C_2^{2-}, CN^-, N_2
(c) CN^-, N_2, O_2^{2-}, CO_2^{2-}
(d) N_2, O_2^-, NO^+, CO

Ans. ***(b)***

Isoelectronic species have same number of electrons, NO^+, C_2^{2-}, CN^- and N_2 all have 14 electrons.

83 Which one of the following pairs of species have the same bond order? **[AIEEE 2008]**

(a) CN^- and NO^+ (b) CN^- and CN^+
(c) O_2^- and CN^- (d) NO^+ and CN^+

Ans. ***(a)***

CN^- and NO^+ both have same number of electrons and same bond order (3).

84 Which of the following species exhibits diamagnetic behaviour? **[AIEEE 2007]**

(a) O_2^{2-} (b) O_2^+ (c) O_2 (d) NO

Ans. ***(a)***

The correct option is O_2^{2-}. This species has 18 electrons, which are filled in such a way that all molecular orbitals are fully filled, so diamagnetic.

$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2$

85 In which of the following ionisation processes, the bond order has increased and the magnetic behaviour has changed? **[AIEEE 2007]**

(a) $C_2 \rightarrow C_2^+$ (b) $NO \rightarrow NO^+$
(c) $O_2 \rightarrow O_2^+$ (d) $N_2 \rightarrow N_2^+$

Ans. ***(b)***

$NO \longrightarrow NO^+ + e^-$

(NO^+) Total electrons = 14

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_z^2 \approx \pi 2p_x^2, \sigma 2p_y^2$

Diamagnetic,

$$\text{Bond order} = \frac{10-4}{2} = 3$$

(NO) Total electrons = 15

$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^{1+1} \approx \pi 2p_y^{1+1}, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y$

Paramagnetic, $\text{Border} = \frac{10-5}{2} = 2.5$

Electron is taken away from non-bonding molecular orbital, that's why bond order increases.

86 Which of the following hydrogen bond is the strongest? **[AIEEE 2007]**

(a) O—H···N (b) F—H···F
(c) O—H···O (d) O—H···F

Ans. ***(b)***

Since, H–bond is the electrostatic force of attraction between H–atom and electronegative element. Thus, fluorine being the most electronegative element forms stronger H–bonds. On the other hand, H–F possesses larger electronegative difference than O–H.

Therefore, H–F molecule is more polarised than O–H, due to which H–atom of H–F bears larger amount of partial charge than that of O–H. This suggests H–atom of H–F attracts more strongly F–atom than that of O–H.

Hence, H–F forms more stronger H–bonds with fluorine than that of O–H.

87 Which of the following molecules/ions does not contain unpaired electrons? **[AIEEE 2006]**

(a) O_2^{2-} (b) B_2 (c) N_2^+ (d) O_2

Ans. ***(a)***

Molecular orbital configuration of given molecules are

O_2^{2-} (Total number of electrons = 18)

$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2$

B_2 (Total number of electrons = 10)

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 \approx \pi 2p_y^1$

N_2^+ (Total number of electrons = 13)

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^1$

O_2 (Total number of electrons = 16)

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^1, \pi^* 2p_x^1$

Thus, O_2^{2-} does not contain any unpaired electron.

88 Increasing order of bond strength of O_2, O_2^-, O_2^{2-} and O_2^+ is **[AIEEE 2002]**

(a) $O_2^+ < O_2 < O_2^- < O_2^{2-}$
(b) $O_2 < O_2^+ < O_2^- < O_2^{2-}$
(c) $O_2^- < O_2^{2-} < O_2^+ < O_2$
(d) $O_2^{2-} < O_2^- < O_2 < O_2^+$

Ans. ***(d)***

Higher the bond order, greater is the bond strength.

Species	Bond order
O_2^{2-}	1
O_2^-	1.5
O_2	2.0
O_2^+	2.5

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05

Chemical Thermodynamics

TOPIC 1

Generalised terms and First Law of Thermodynamics

01 For water $\Delta_{vap}H = 41 kJ\ mol^{-1}$ at 373 K and 1 bar pressure. Assuming that water vapour is an ideal gas that occupies a much larger volume than liquid water, the internal energy change during evaporation of water is ..... kJ mol^{-1}.

[Use $R = 8.3\ J\ mol^{-1}\ K^{-1}$]

[2021, 26 Aug Shift-II]

Ans. ***(38)***

$H_2O(l) \longrightarrow H_2O(g)$

$\because\ \Delta H = \Delta U + \Delta n_g RT$

ΔH = enthalpy of vaporisation

ΔU = change in internal energy

Δn_g = number of moles of water vapour

$R = 8.3\ J\ mol^{-1}\ K^{-1}$

$T = 373\ K$

$\therefore 41 kJ = \Delta U + RT$

$\Delta U = 41 - 8.3 \times 373 \times 10^{-3} = 41 - 3.095$

$= 37.90\ kJ\ mol^{-1} = 38\ kJ\ mol^{-1}$

02 A system does 200 J of work and at the same time absorbs 150 J of heat. The magnitude of the change in internal energy is ..... J. (Nearest integer)

[2021, 25 July Shift-II]

Ans. ***(50)***

Work done by the system, $W = -200\ J$

Heat absorbed, $q = +150\ J$

According to first law of thermodynamics internal energy,

$\Delta U = q + W$

$\Delta U = 150 + (-200)$

{ΔU = Change in internal energy}

$= -50\ J$

Magnitude $= |-50\ J| = |\Delta U|$

$= 50\ J$

03 At 25°C, 50 g of iron reacts with HCl to form $FeCl_2$. The evolved hydrogen gas expands against a constant pressure of 1 bar. The work done by the gas during this expansion is ..... J. (Round off to the nearest integer)

[Given, $R = 8.314\ J\ mol^{-1}\ K^{-1}$. Assume, hydrogen is an ideal gas]

[Atomic mass off Fe is 55.85 u]

[2021, 16 March Shift-II]

Ans. ***(2218)***

$\underset{50\ g}{Fe(s)} + HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g)$

(Moles of Fe = Moles of H_2)

$\text{moles} = \frac{50}{55.85} \quad 0.8952\ \text{mol} \quad 0.8952\ \text{mol}$

$= 0.8952\ mol$

Work done can be given by

$W = -p_{ext}\Delta V = -\Delta n_g RT$

where, Δn_g = {gaseous moles on product side} –

{gaseous mole on reactant side}

$= 0.8952 - 0$

$W = -0.8952 \times 8.314 \times 298$

$= -2217.92\ J$

Closest integer = 2218

04 Five moles of an ideal gas at 293 K is expanded isothermally from an initial pressure of 2.1 MPa to 1.3 MPa against at constant external pressure 4.3 MPa. The heat transferred in this process is ..... kJ mol^{-1}. (Rounded off to the nearest integer)

[$R = 8.314\ J\ mol^{-1}K^{-1}$]

[2021, 25 Feb Shift-II]

Ans. ***(15)***

The gas performs isothermal irreversible work (W).

where, $\Delta U = 0$ (change in internal energy)

From, 1st law of thermodynamics,

$\Rightarrow \quad \Delta U = \Delta Q + W$

$\Rightarrow \quad 0 = \Delta Q + W$

$\Rightarrow \quad \Delta Q = -W$

Now, $W = -p_{ext}(V_2 - V_1)$

$= -p_{ext}\left(\frac{nRT}{p_2} - \frac{nRT}{p_1}\right)$

$= -p_{ext} \times nRT\left(\frac{1}{p_2} - \frac{1}{p_1}\right)$

Given, $p_{ext} = 4.3$ MPa, $p_1 = 2.1$ MPa,

$p_2 = 1.3$ MPa,

$n = 5$ mol,

$T = 293\ K$

and $R = 8.314\ J\ mol^{-1}\ K^{-1}$

$= -4.3 \times 5 \times 8.314 \times 293\left(\frac{1}{1.3} - \frac{1}{2.1}\right)$

$= -15347.70\ J\ mol^{-1}$

$= -15.347\ kJ\ mol^{-1}$

$\simeq -15\ kJ\ mol^{-1}$

$\Rightarrow \quad \Delta Q = 15\ kJ\ mol^{-1}$

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05 The ionisation enthalpy of Na^+ formation from Na(*g*) is 495.8 kJ mol^{-1}, while the electron gain enthalpy of Br is –325.0 kJ mol^{-1}. Given, the lattice enthalpy of NaBr is –728.4 kJ mol^{-1}. The energy for the formation of NaBr ionic solid is (–) ..... $\times 10^{-1}$ kJ mol^{-1}.

[2021, 25 Feb Shift-I]

Ans. ***(5576)***

$$Na(g) \xrightarrow{IE_1} Na^+(g) \quad [IE_1 = 495.8\ kJ\ mol^{-1}]$$

$$Br(g) \xrightarrow[\text{gain enthalpy}]{\text{Electron}} (EG)\ Br^-(g)\ [\text{Gain enthalpy} = -325\ kJ\ mol^{-1}]$$

$$Na^+ + Br^- \xrightarrow[\text{energy}]{\text{Lattice}} (LE)\ NaBr(s) \quad [\text{Lattice energy} = -728.4\ kJ\ mol^{-1}]$$

$\Delta H_{Formation} = IE_1 + \text{Gain enthalpy} + \text{Lattice energy}$

$\Delta H = 495.8 + (-325) + (-728.4)$

$= -557.6$ kJ/mol

$= -5576 \times 10^{-1}$ kJ

06 Five moles of an ideal gas at 1 bar and 298 K is expanded into vacuum to double the volume. The work done is **[2020, 4 Sep Shift-II]**

(a) $-RT \ln V_2/V_1$ (b) $-RT(V_2 - V_1)$

(c) $C_V(T_2 - T_1)$ (d) zero

Ans. ***(d)***

Expansion of a gas in vacuum ($p_{ext} = 0$) is called free expansion. No work is done during free expansion, since as the expansion is done in vacuum that is in absence of external pressure, hence *w* will be

$$w = -p_{ext}\Delta V \Rightarrow w = 0$$

(Here, $p_{ext} = 0$), because expansion takes place in vacuum)

07 The internal energy change (in J) when 90 g of water undergoes complete evaporation at 100°C is ....., (Given : ΔH_{vap} for water at 373 K = 41kJ/mol, $R = 8.314\ JK^{-1}mol^{-1}$)

[2020, 5 Sep Shift-I]

Ans. ***(189494)***

Given, $dH = 41$ kJ/mol $= 41 \times 1000 \times 5$ J [For 90 g or 5 mol $H_2O(l)$]

$$H_2O(l) \longrightarrow H_2O(g)$$

$t = 0$	$\frac{90}{18}$ mol	–
$t = \infty$	0	5 mol

$\Rightarrow \quad \Delta n_g = 5 \quad \because T = 373$ K

We know that,

$dH = dU + \Delta n_g RT$

dU = Internal energy change

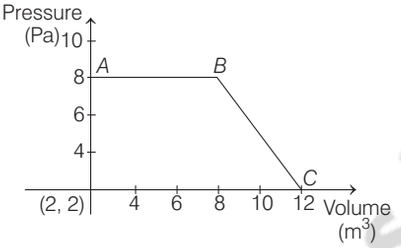
$= dH - \Delta n_g RT$

$= 41 \times 1000 \times 5 - 5 \times 8.314 \times 373$

$= 189494.39$ J $\simeq 189494.00$ J

08 The magnitude of work done by a gas that undergoes a reversible expansion along the path *ABC* shown in the figure is ..... .

[2020, 8 Jan Shift-I]



Ans. ***(48.00)***

Work done is equal to the area under *pV*-curve.

$\therefore$ Work done $(|W|) = \frac{1}{2}(6+10) \times 6$

$= 48.00$ Pa. $m^3 = 48.00$ J.

09 At constant volume, 4 mol of an ideal gas when heated from 300 K to 500 K changes its internal energy by 5000 J. The molar heat capacity at constant volume is ..... **[2020, 8 Jan Shift-II]**

Ans. ***(6.25)***

Given: $n = 4$ mol

$\Delta T = 500\ K - 300\ K = 200\ K$

$\Delta U = 5000$ J

$\Delta U = nC_V\Delta T$

$$C_V = \frac{\Delta U}{n\Delta T} = \frac{5000}{4 \times 200} = \frac{50}{8} = 6.25$$

10 Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas? (Assume non- expansion work is zero)

[2019, 8 April Shift-I]

(a) Cyclic process : $q = -W$

(b) Adiabatic process : $\Delta U = -W$

(c) Isochoric process : $\Delta U = q$

(d) Isothermal process : $q = -W$

Ans. ***(b)***

From the 1st law of thermodynamics,

$$\Delta U = q + W$$

where, ΔU = change in internal energy

q = heat, W = work done

The above equation can be represented for the given processes involving ideal gas as follows:

(a) **Cyclic process** For cyclic process, $\Delta U = 0$

$\therefore \quad q = -W$

Thus, option (a) is correct.

(b) **Adiabatic process** For adiabatic process, $q = 0 \Rightarrow \Delta U = W$

Thus, option (b) is incorrect.

(c) **Isochoric process** For isochoric process, $\Delta V = 0$. Thus, $W = 0 (\because W = p\Delta V)$.

$\therefore \quad \Delta V = q$

Thus, option (c) is correct.

(d) **Isothermal process** For isothermal process, $\Delta U = 0$

$\therefore \quad q = -W$

Thus, option (d) is correct.

11 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28\ JK^{-1}\ mol^{-1}$, calculate ΔU and ΔpV for this process. ($R = 8.0\ JK^{-1}\ mol^{-1}$)

[2019, 8 April Shift-II]

(a) $\Delta U = 2.8$ kJ; $\Delta(pV) = 0.8$ kJ

(b) $\Delta U = 14$ J; $\Delta(pV) = 0.8$ J

(c) $\Delta U = 14$ kJ; $\Delta(pV) = 4$ kJ

(d) $\Delta U = 14$ kJ; $\Delta(pV) = 18$ kJ

Ans. ***(c)***

Given, $n = 5$ mol, $T_2 = 200$ K, $T_1 = 100$ K

$C_V = 28\ JK^{-1}\ mol^{-1}$

$\Delta U = nC_V\Delta T = nC_V(T_2 - T_1)$

$= 5\ mol \times 28\ JK^{-1}\ mol^{-1} \times (200 - 100)\ K$

$= 14{,}000\ J = 14\ kJ$

$\Delta pV = nR\Delta T = nR(T_2 - T_1)$

$= 5\ mol \times 8\ JK^{-1}\ mol^{-1} \times (200 - 100)\ K$

$= 4000\ J = 4\ kJ$

12 Among the following the set of parameters that represents path functions, is **[2019, 9 April Shift-I]**

(A) $q + W$ (B) q

(C) W (D) $H - TS$

(a) (A) and (D) (b) (A), (B) and (C)

(c) (B), (C) and (D) (d) (B) and (C)

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Ans. ***(d)***

q (heat) and W (work) represents path functions. These variables are path dependent and their values depends upon the path followed by the system in attaining that state. They are inexact differentials whose integration gives a total quantity depending upon the path.

Option (a), i.e. $q + W$ and option (d), i.e. $H-TS$ are state functions. The value of state functions is independent to the way in which the state is attained. All the state functions are exact differentials and cyclic integration involving a state functions is zero.

13 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume $10\,m^3$ at 1000 K. Given R is the gas constant in $JK^{-1}\,mol^{-1}$, x is **[2019, 9 Jan Shift-I]**

(a) $\frac{2R}{4-R}$ (b) $\frac{4-R}{2R}$ (c) $\frac{4+R}{2R}$ (d) $\frac{2R}{4+R}$

Ans. ***(b)***

From the ideal gas equation,

$$pV = \Sigma nRT \quad ...(i)$$

Given: $p = 200\,Pa$, $V = 10\,m^3$, $T = 1000\,K$

$n_A = 0.5$ moles, $n_B = x$ moles

On substituting the given values in equation (i), we get

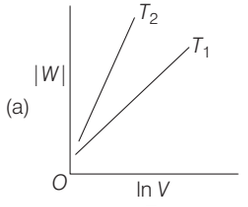
$$200 \times 10 = (n_A + n_B) \times R \times 1000$$

$$0.5 + x = \frac{200 \times 10}{R \times 1000}$$

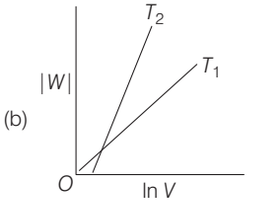
$$\frac{1}{2} + x = \frac{2}{R} = \frac{2}{R} - \frac{1}{2} = \frac{4-R}{2R}$$

14 Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temp. T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (W) on the final volume (V) is **[2019, 9 Jan Shift-I]**

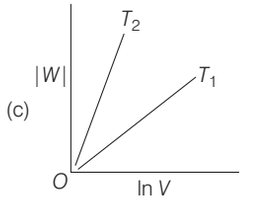
(a)



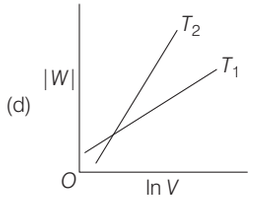
(b)



(c)



(d)



Ans. ***(c)***

For isothermal reversible expansion,

$$|W| = nRT \ln \frac{V_f}{V_i}$$

$$= nRT \ln \frac{V}{V_i}$$

where, V = final volume, V_i = initial final.

or $|W| = nRT \ln V - nRT \ln V_i$

On comparing with equation of straight line, $y = mx + c$, we get

$$\text{slope} = m = + nRT$$

$$\text{intercept} = - nRT \ln V_i$$

Thus, plot of $|W|$ with $\ln V$ will give straight line in which slope of 2(T_2) is greater than slope of 1(T_1) which is given in all options.

Now, if $V_i < 1$ then y intercept ($- nRT\,V_i$) becomes positive and if it is positive for one case then it is positive for other case also. Thus, it is not possible that one y-intercept goes above and other y-intercept goes below. Thus, option (b) and (d) are incorrect.

If we extent plot given in option (a) it seems to be merging which is not possible because if they are merging they give same +ve y-intercept. But they cannot give same y-intercept because value of T is different.

Now, if we extent the line of T_1 and T_2 given in option (c) it seems to be touching the origin. If they touch the origin then y-intercept becomes zero which is not possible. Thus, it is not the exactly correct answer but among the given options it is the most appropriate one.

15 An ideal gas undergoes isothermal compression from $5\,m^3$ to $1\,m^3$ against a constant external pressure of $4\,Nm^{-2}$. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J $mol^{-1}K^{-1}$, the temperature of Al increases by **[2019, 10 Jan Shift-II]**

(a) $\frac{3}{2}$ K (b) 1 K

(c) 2 K (d) $\frac{2}{3}$ K

Ans. ***(d)***

It is an irreversible isothermal compression of an ideal gas.

(i) $dE = dq + p(V_f - V_i)$

where, dE = Internal energy change

dq = amount of heat released

$\Rightarrow \quad 0 = dq + p(V_f - V_i)$

[$\because dE = 0$ for an isothermal process]

$\Rightarrow \quad dq = -4(1-5) = 16\,J$

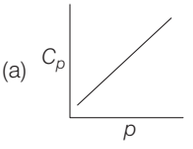
(ii) $dq = n \times C \times \Delta T$ (for Al)

$\Rightarrow 16\,J = 1\,mol \times 24\,J\,mol^{-1}\,K^{-1} \times \Delta T$

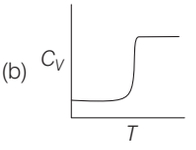
$\Rightarrow \quad \Delta T = \frac{16}{24}\,K = \frac{2}{3}\,K$

16 For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?

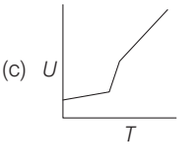
(a)



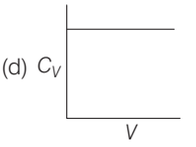
(b)



(c)



(d)



[2019, 12 Jan Shift-I]

Ans. ***(a)***

For diatomic ideal gases,

$$C_V = \frac{f}{2}R \text{ and } C_p = \left(\frac{f}{2} + 1\right)R$$

where, f = degree of freedom

f = translational degree of freedom + degree of freedom

$= 3 + 2 = 5$ [at normal temperature]

The explanation of various plots are as follows.

(a) We know that, C_p is heat capacity at constant pressure. Thus, it does not vary with the variation in pressure. Hence, plot given in option (a) is incorrect.

(b) In this plot, C_V first increases slightly with increase in

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temperature and then increases sharply with temperature. The sharp increase is due to increase in degree of freedom.

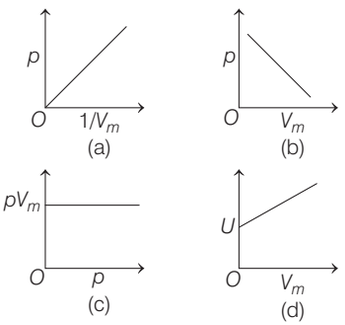
Thus, plot given in option (b) is correct.

(c) For ideal gases, Internal energy $(U) \propto T$

Thus, as temperature increases internal energy also increases. As temperature increases further degree of freedom also increases thus, there is slight variation in the graph. First translational degree of freedom is present followed by rotational and vibrational degree of freedom. Hence, plot given in option (c) is also correct.

(d) C_V is heat capacity at constant volume. Thus, it does not vary with variation in volume. Hence, plot given in option (d) is correct.

17 The combination of plots which does not represent isothermal expansion of an ideal gas is **[2019, 12 Jan Shift-II]**



Ans. ***(c)***

In isothermal expansion, $pV_m = K$ (constant)

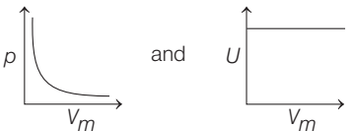
This relation is plotted in graph '*C*'

Likewise, $p = \frac{K}{V_m}$

This relation is plotted in graph "*A*".

Thus, graph *B* and *D* are incorrect.

For them the correct graphs are:



for graph *B* for graph *D*

18 ΔU is equal to **[JEE Main 2017]**

(a) isochoric work (b) isobaric work
(c) adiabatic work (d) isothermal work

Ans. ***(c)***

According to first law of thermodynamics,

$$\Delta U = q + W = q - p\Delta V$$

In isochoric process $(\Delta V = 0)$, $\Delta U = q$

In isobaric process $(\Delta p = 0)$, $\Delta U = q$

In adiabatic process $(q = 0)$, $\Delta U = W$

In isothermal process $(\Delta T = 0)$ and $\Delta U = 0$

$\therefore$ ΔU is equal to adiabatic work.

19 A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be (R = 8.314 J / mol K, ln 7.5 = 2.01) **[JEE Main 2013]**

(a) $q = +208$ J, $W = -208$ J
(b) $q = -208$ J, $W = -208$ J
(c) $q = -208$ J, $W = +208$ J
(d) $q = +208$ J, $W = +208$ J

Ans. ***(a)***

As the process is carrying out at constant temperature, therefore this type of expansion is called isothermal reversible expansion, for which, $\Delta U = 0$.

Hence, $q = -W$

i.e., heat absorbed by the system is equal to the work done by the system.

Thus, $q = +208$ J, $W = -208$ J

20 An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, then which of the following statements is correct ? **[AIEEE 2006]**

(a) $(T_f)_{irrev} > (T_f)_{rev}$
(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
(c) $(T_f)_{rev} = (T_f)_{irrev}$
(d) $T_f = T_i$ for both reversible and irreversible processes

Ans. ***(a)***

In an ideal gas, there are no intermolecular forces of attraction.

Hence, $T_f = T_i$ for both reversible and irreversible processes.

21 An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is **[AIEEE 2004]**

(a) −900 J (b) −900 kJ
(c) 270 kJ (d) 900 kJ

Ans. ***(a)***

Work done due to change in volume against constant pressure is

$W = -p(V_2 - V_1)$

$= -1 \times 10^5$ Nm^{-2} $(1 \times 10^{-2} - 1 \times 10^{-3})$ m^3

$= -900$ Nm $= -900$ J [1 Nm = 1 J]

22 The internal energy change when a system goes from state *A* to *B* is 40 kJ/mol. If the system goes from *A* to *B* by a reversible path and returns to state *A* by an irreversible path, what would be the net change in internal energy? **[AIEEE 2003]**

(a) 40 kJ (b) >40 kJ
(c) <40 kJ (d) zero

Ans. ***(d)***

$\Delta E = 0$, in a cyclic process.

23 Heat required to raise the temperature of 1 mole of a substance by 1° is called **[AIEEE 2002]**

(a) specific heat
(b) molar heat capacity
(c) water equivalent
(d) specific gravity

Ans. ***(b)***

The amount of heat required to raise the temperature of one mole of substance through 1°C is called molar heat capacity.

$$C = \frac{q}{T_2 - T_1}$$

24 A heat engine absorbs heat q_1 from a source at temperature T_1 and heat q_2 from a source at temperature T_2. Work done is found to be $J(q_1 + q_2)$. This is in accordance with **[AIEEE 2002]**

(a) First law of thermodynamics
(b) Second law of thermodynamics
(c) Joules equivalent law
(d) None of the above

Ans. ***(c)***

Joules law suggests

$$J = \frac{\text{Mechanical work done by the system, } W}{\text{Net heat given to the system, } Q}$$

Hence, $J = \frac{W}{q_1 + q_2}$

Therefore, $W = J(q_1 + q_2)$

is constant with Joules law of equivalence.

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TOPIC 2
Reactions Related to Enthalpies and Hess's Law

25 200 mL of 0.2 M HCl is mixed with 300 mL of 0.1 M NaOH. The molar heat of neutralisation of this reaction is – 57.1 kJ. The increase in temperature in °C of the system on mixing is $x \times 10^{-2}$.

The value of x is ..... (Nearest integer)

[Given, specific heat of water = 4.18 J g^{-1} K^{-1}

Density of water = 1.00 g cm^{-3}]

(Assume no volume change on mixing) **[2021, 27 Aug Shift-I]**

Ans. ***(82)***

Millimoles of HCl = $200 \times 0.2 = 40$

Millimoles of NaOH = $300 \times 0.1 = 30$

Heat released (q) = $n \times$ molar heat

$$= \frac{30}{1000} \times 57.1 \times 1000 = 1713 \text{ J}$$

Mass of solution = $500 \times 1 = 500$ g

We know that,

$$\Delta T = \frac{q}{mc} = \frac{1713 \text{ J}}{500 \text{ g} \times 4.18 \text{ J/g-K}}$$

$$= 0.8196 \text{ K} = 81.96 \times 10^{-2} \text{ K}$$

$$x \approx 82$$

26 When 400 mL of 0.2 M H_2SO_4 solution is mixed with 600 mL of 0.1 M NaOH solution, the increase in temperature of the final solution is ..... $\times 10^{-2}$ K. (Round off to the nearest integer).

[Use : $H^+(aq) + OH^+(aq) \longrightarrow H_2O$; $\Delta_y H = -57.1 \text{ kJ mol}^{-1}$]

Specific heat of H_2O = 0.18 J K^{-1} g^{-1}, density of H_2O = 1.0 g cm^{-3}.

Assume no change in volume of solution on mixing. **[2021, 27 July Shift-II]**

Ans. ***(82)***

$$\text{Molarity} = \frac{n \times 1000}{V(\text{mL})}$$

where, n = number of moles

V = volume of solution in mL

$$\text{Moles} = \frac{\text{molarity} \times \text{volume (mL)}}{1000}$$

1 mole of H_2SO_4 produces 2 moles of H^+

$$n_{H^+} = \frac{400 \times 0.2}{1000} \times 2 = 0.16 \text{ moles}$$

and 1 mole of NaOH produces 1 mole of OH^-.

$$n_{OH^-} = \frac{600 \times 0.1}{1000} = 0.06$$

n_{OH^-} is low.

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

Mol : 1 2 1 2

Now, 1 mole H_2SO_4 requires 2 moles NaOH, then 0.06 mole of NaOH will require = 0.03 moles of H_2SO_4

$\therefore$ 0.06 mole of OH^- reacts with 0.06 mole of H^+.

$$m = 1 \times 1000$$

Now, heat liberated from reaction = heat gained by solution.

$$n \times \Delta H = m \times C_p \times \Delta T$$

$$0.06 \times 57.1 \times 10^3 = (1000 \times 1) \times 4.18 \times \Delta T$$

$$\Rightarrow \quad \Delta T = 0.8196 \text{ K} = 82 \times 10^{-2} \text{ K}$$

27 For water at 100°C and 1 bar, $\Delta_{vap} H - \Delta_{vap} U =$ ..... $\times 10^2$ J mol^{-1}.

(Round off to the nearest integer)

[Use : $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$]

[Assume volume of $H_2O(l)$ is much smaller than volume of $H_2O(g)$. Assume $H_2O(g)$ treated as an ideal gas] **[2021, 27 July Shift-I]**

Ans. ***(31)***

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Using formula, $\Delta H = \Delta U + \Delta n_g RT$

For 1 mole water,

$$\Delta n_g = 1$$

$$\therefore \Delta n_g RT = 1 \text{ mol} \times 8.31 \text{ J/mol K} \times 373 \text{ K}$$

$$= 3099.63 \text{ J} \simeq 31 \times 10^2 \text{ J}$$

28 The Born-Haber cycle for KCl is evaluated with the following data :

$\Delta_f H°$ for KCl = – 436.7 kJ mol^{-1}

$\Delta_{sub} H°$ for K = 89.2 kJ mol^{-1},

$\Delta_{ionisation} H°$ for K = 419.0 kJ mol^{-1};

$\Delta_{electron\ gain} H°$ for Cl(g) = – 348.6 kJ mol^{-1}, $\Delta_{bond} H°$ for Cl_2 = 243.0 kJ mol^{-1}

The magnitude of lattice enthalpy of KCl in kJ mol^{-1} is .....

(Nearest integer) **[2021, 26 Aug Shift-I]**

Ans. ***(718)***

Born-Haber cycle for KCl is as follows

$$K_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow KCl(s);\ \Delta H°_f$$

$\Delta H_{sublimation}$ ↓ ; ↓ $\Delta H_{dissociation}$

$$K_{(g)} \quad Cl_{(g)}$$

IE_1 ↓ ; ↓ EA

$$K^+_{(g)} + Cl^-_{(g)} \longrightarrow KCl(s),\ \Delta H°_{lattice}$$

$$\therefore\ \Delta H°_f = \Delta H_{sublimation} + \frac{1}{2}\Delta H_{dissociation} + IE_1 + EA + \Delta H_{lattice}$$

$$-436.7 \text{ kJ/mol} = 89.2 \text{ kJ/mol} + \frac{1}{2} \times (243 \text{ kJ/mol}) + 419 \text{ kJ/mol} + (-348.6 \text{ kJ/mol}) + \Delta H°_{lattice}$$

$$\Rightarrow \quad \Delta H°_{lattice} = -717.8 \text{ kJ/mol}$$

$\therefore$ Magnitude of lattice enthalpy of KCl in kJ/mol is 718 (nearest).

29 At 298 K, the enthalpy of fusion of a solid (X) is 2.8 kJ mol^{-1} and the enthalpy of vaporisation of the liquid (X) is 98.2 kJ mol^{-1}. The enthalpy of sublimation of the substance (X) in kJ mol^{-1} is ..... . (Nearest integer) **[2021, 25 July Shift-I]**

Ans. ***(101)***

Given,

Enthalpy of fusion,

$$\Delta H_{fus} = 2.8 \text{ kJ mol}^{-1}$$

Enthalpy of vaporisation,

$$\Delta H_{vap} = 98.2 \text{ kJ mol}^{-1}$$

Solid $\xrightarrow{\Delta H_{fus}}$ Liquid $\xrightarrow{\Delta H_{vap}}$ Gas

ΔH_{sub}

Using Hess's law,

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

$$= 2.8 + 98.2$$

$$= 101 \text{ kJ/mol}$$

30 At 298.2 K the relationship between enthalpy of bond dissociation (in kJ mol^{-1}) for hydrogen (E_H) and its isotope, deuterium (E_D), is best described by **[2021, 25 July Shift-I]**

(a) $E_H = \frac{1}{2}E_D$ (b) $E_H = E_D$

(c) $E_H \simeq E_D - 7.5$ (d) $E_H = 2E_D$

Ans. ***(c)***

Enthalpy of bond dissociation (kJ/mol) at 298.2 K

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For hydrogen = 435.88 kJ/mol

For deuterium = 443.35 kJ/ mol

Hence, difference in energy of deuterium and hydrogen is approx. 7.50 kJ/mol

Therefore, equation is $[E_H \simeq E_D - 7.5]$

Here, deuterium is a heavy isotope of hydrogen that's why they required more enthalpy of bond dissociation, i.e. 7.5 kJ/mol.

31 If the standard molar enthalpy change for combustion of graphite powder is -2.48×10^2 kJ mol^{-1}, the amount of heat generated on combustion of 1 g of graphite powder is ..... kJ. (Nearest integer)

[2021, 22 July Shift-II]

Ans. ***(21)***

Standard molar enthalpy change for combustion of graphite powder, i.e. carbon-12 is -2.48×10^2 kJ mol^{-1}.

So, heat generated of 1g of graphite powder

$$= \frac{2.48\times10^2}{12}$$

$$= 20.66 = 21 \text{ kJ}.$$

Hence, amount of heat generated is 21 kJ.

32 For the reaction,

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

the reaction enthalpy $\Delta_r H =$ ..... kJ mol^{-1}

(Round off to the nearest integer).

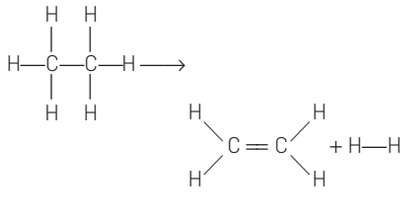
[Given : Bond enthalpies in kJ mol^{-1} :

C—C = 347, C=C = 611; C—H = 414; H—H = 436]

[2021, 18 March Shift-I]

Ans. ***(128)***

The equation representing various substances involved in chemical reaction is



Given bond enthalpies of various bonds in kJ mol^{-1} i.e. C—C = 347, C=C = 611, C—H = 414, H—H = 436

This reaction involves the breaking of 2C—H bonds and formation, of 1 C = C bond and 1 H—H bond.

$\Delta_r H =$

[Sum of bond ethalpies ofreactants]

$-$ [Sum of bond enthalpies of products]

$= [1\Delta_{C-C}H + 6\Delta_{C-H}H]$

$- [1\Delta_{C=C}H + 4\Delta_{C-H}H + 1\Delta_{H-H}H]$

$= (357 + 6\times414) - [611 + 4\times414 + 436]$

$= 2831 - 2703$

$= 128$ kJ/mol.

33 The standard enthalpies of formation of Al_2O_3 and CaO are -1675 kJ mol^{-1} and -625 kJ mol^{-1} respectively.

For the reaction,

$3CaO + 2Al \longrightarrow 3Ca + Al_2O_3$ the standard reaction enthalpy $\Delta_r H°$ ..... kJ.

(Round off to the nearest integer).

[2021, 17 March Shift-I]

Ans. ***(230)***

Given, $\Delta_f H^\circ_{Al_2O_3} = -1675$ kJ/mol

$\Delta_f H^\circ_{CaO} = -625$ kJ/mol

To find $\Delta_r H^\circ$ for the reaction

$3CaO + 2Al \longrightarrow 3Ca + Al_2O_3$; $\Delta_r H^\circ = ?$

$\Delta_r H^\circ = \Sigma\Delta_f H^\circ_{Product} - \Sigma\Delta_f H^\circ_{Reactant}$

$= \{\Delta_f H^\circ_{Al_2O_3} + 3\Delta_f H^\circ_{Ca}\}$

$- \{3\Delta_f H^\circ_{CaO} + 2\Delta_f H^\circ_{Al}\}$

$= \Delta H_f^\circ(Al_2O_3) - 3\times\Delta H_f^\circ(CaO)$

We know, $\Delta_f H^\circ$ for elemental state = 0

$\Rightarrow \Delta_f H^\circ_{Ca} = 0, \Delta_f H^\circ_{Al} = 0$

Putting the value,

$\Delta_r H^\circ = \{-1675 + 0\} - \{3(-625) + 0\}$

$= -1675 + 1905 = 230$ kJ

34 The average S—F bond energy in kJ mol^{-1} of SF_6 is .....

(Rounded off to the nearest integer) [Given, the values of standard enthalpy of formation of $SF_6(g)$, $S(g)$ and $F(g)$ are -1100, 275 and 80 kJ mol^{-1} respectively.]

[2021, 26 Feb Shift-II]

Ans. ***(309)***

$$S(g) + 6F(g) \longrightarrow SF_6(g)$$

So, $\Delta_f H°[S, g] + 6\times\Delta_f H°[F, g]$

$= \Delta_f H°[SF_6, g] + 6\times E_{S-F}$

$[\therefore E_{S-F}$ = Average S—F bond energy in $SF_6]$

$275 + 6\times80 = -1100 + 6\times E_{S-F}$

$\Rightarrow E_{S-F} = \dfrac{275 + 6\times80 + 1100}{6}$

$= 309.16$ kJ mol^{-1} $= 309$ kJ mol^{-1}

35 Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol^{-1} and 4 kJ mol^{-1}, respectively. The hydration enthalpy of NaCl is

[2020, 5 Sep Shift-II]

(a) -780 kJ mol^{-1} (b) 780 kJ mol^{-1}

(c) -784 kJ mol^{-1} (d) 784 kJ mol^{-1}

Ans. ***(c)***

The enthalpy of solution of an ionic solid is numericlly equal to the sum of its hydration and lat energies,

i.e. $\Delta H^\circ_{sol} = \Delta H^\circ_{hydration} + \Delta H^\circ_{lattice}$

$\therefore$ NaCl (s) $\xrightarrow{\Delta H = 4}$ NaCl (*aq*)

$\Delta H° = 788 \searrow \quad \nearrow \Delta H°_{hyd}$

$Na^+(g) + Cl^-(g)$

$\Delta_{sol}H° = \Delta_{lattice}H° + \Delta_{hyd}H°$

$4 = 788 + \Delta_{hyd}H°$

$\Delta H_{hyd}H° = -784$ kJ/mol

36 The standard heat of formation ($\Delta_f H^\circ_{298}$) of ethane (in kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are -1560, -393.5 and -286 kJ/mol, respectively is .....

[2020, 7 Jan Shift-II]

Ans. ***(192.50)***

$\Delta_f H°$ of ethane is $\Delta H°$ of the reaction :

$2C(\text{graphite}) + 3H_2(g) \longrightarrow C_2H_6(g)$

From $\Delta_c H°$ (heat of combustion) values,

$\Delta_f H° = (2\times\Delta_c H°$ of graphite)

$+ (3\times\Delta_c H°$ of $H_2) - (\Delta_c H°$ of $C_2H_6)$

$= (-2\times286) + (-393.5\times3)$

$- (-1560)$ kJ mol^{-1}

$= -192.50$ kJ mol^{-1}

37 The heat of combustion of ethanol into carbon dioxides and water is -327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is (R = 2 cal mol^{-1} K^{-1}) .....

[2020, 2 Sep Shift-II]

Ans. ***(326400)***

The combustion equation of ethanol (C_2H_5OH or C_2H_6O) is

$$C_2H_6O(l) + \left(2 + \frac{6}{9} - \frac{1}{2}\right)O_2(g) \xrightarrow{300K}$$

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$$2CO_2(g) + \frac{6}{2}H_2O(l)$$

or $C_2H_6O(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta n_g = (2+0) - (0+3) = -1$

$\Rightarrow dq_p = du_v + \Delta n_g RT$

$\Rightarrow du_v = dq_p - \Delta n_g RT$

$= -327 - (-1) \times (2 \times 10^{-3}) \times 300$

$= -326.400$ kcal $= -326400$ cal

$\because dq_p$ = Heat at constant pressure or enthapy change

dU_v = Heat at constant volume or internal energy change

38 If enthalpy of atomisation for $Br_2(l)$ is x kJ/mol and bond enthalpy for Br_2 is y kJ/mol, the relation between them **[2020, 9 Jan Shift-II]**

(a) is $x < y$ (b) does not exist

(c) is $x > y$ (d) is $x = y$

Ans. ***(c)***

Atomisation of $Br_2(l)$

$Br_2(l) \longrightarrow 2Br(g)$; $\Delta H = x$ kJ mol^{-1}

which can be considered as sum of following :

$Br_2(l) \longrightarrow Br_2(g)$;

ΔH = a positive value ...(i) (endothermic process)

$Br_2(g) \longrightarrow 2Br(g)$; ΔH (bond enthalpy of Br_2) $= y$ ...(ii)

$\therefore x = y +$ (Positive value), and $x > y$.

39 For silver, C_p (J K^{-1}mol^{-1}) $= 23 + 0.01$T. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of ΔH will be close to **[2019, 8 April Shift-I]**

(a) 62 kJ (b) 16 kJ

(c) 21 kJ (d) 13 kJ

Ans. ***(a)***

According to Kirchoff's relation,

$$\Delta H = n\int_{T_1}^{T_2} C_p dT \quad ...(i)$$

where, ΔH = Change in enthalpy.

C_p = Heat capacity at constant pressure.

Given, $n = 3$ moles,

$T_1 = 300$ K,

$T_2 = 1000$ K,

$C_p = 23 + 0.01$T

On substituting the given values in Eq. (i), we get

$$\Delta H = 3\int_{300}^{1000} (23 + 0.01T)dT$$

$$= 3\int_{300}^{1000} 23dT + 0.01T\,dT$$

$$= 3\left[23T + \frac{0.01T^2}{2}\right]_{300}^{1000}$$

$$= 3\left[23(1000-300) + \frac{0.01}{2}(1000^2 - 300^2)\right]$$

$= 3[16100 + 4550] = 61950$ J ≈ 62 kJ

40 The difference between ΔH and ΔU ($\Delta H - \Delta U$), when the combustion of one mole of heptane (l) is carried out at a temperature T, is equal to **[2019, 10 April Shift-II]**

(a) $-4RT$ (b) $3RT$

(c) $4RT$ (d) $-3RT$

Ans. ***(a)***

Key Idea The relation between ΔH and ΔU is

$$\Delta H = \Delta U + \Delta n_g RT$$

where, $\Delta n_g = \Sigma n_p - \Sigma n_R$

= number of moles of gaseous products – number of moles of gaseous reactants.

The general combustion reaction of a hydrocarbon is as follows :

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

For heptane, $x = 7$, $y = 16$

$\Rightarrow C_7H_{16}(l) + 11O_2(g) \longrightarrow 7CO_2(g) + 8H_2O(l)$

$\therefore \quad \Delta n_g = 7 - 11 = -4$

Now, from the principle of thermochemistry,

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Rightarrow \quad \Delta H - \Delta U = \Delta n_g RT = -4RT$$

41 Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C. If specific heat of $I_2(s)$ and I_2(vap.) are 0.055 and 0.031 cal g^{-1} K^{-1} respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is **[2019, 12 April Shift-I]**

(a) 2.85 (b) 5.7

(c) 22.8 (d) 11.4

Ans. ***(c)***

Key Idea When q is the amount of heat involved in a system then at constant pressure

$$q = q_p$$

and $\quad C_p\Delta T = \Delta H$

Given reaction :

$$I_2(s) \longrightarrow I_2(g)$$

Specific heat of $I_2(s) = 0.055$ cal g^{-1} K^{-1}.

Specific heat of

I_2(vap)$= 0.031$ cal g^{-1}K^{-1}.

Enthalpy (H_1) of sublimation of iodine $= 24$ cal g^{-1}

If q is the amount of heat involved in a system then at constant pressure $q = q_p$ and

$$\Delta H = C_p\Delta T$$

$$H_2 - H_1 = C_p(T_2 - T_1)$$

$$H_2 = H_1 + \Delta C_p(T_2 - T_1)$$

$$H_2 = 24 + (0.031 - 0.055)(250 - 200)$$

$$H_2 = 24 + (-0.024)(50)$$

$$= 24 - 1.2 = 22.8 \text{ cal/g}$$

Thus, the enthalpy of sublimation of iodine at 250 is 22.8 cal/g.

42 Given :

(i) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$; $\Delta_r H^\ominus = x$ kJ mol^{-1}

(ii) $C(\text{graphite}) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\ominus = y$ kJ mol^{-1}

(iii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$; $\Delta_r H^\ominus = z$ kJ mol^{-1}

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct?

(a) $y = 2z - x$ (b) $x = y - z$

(c) $z = x + y$ (d) $x = y + z$ **[2019, 12 Jan Shift-II]**

Ans. ***(d)***

Second equation given in this question is wrong. Hence, No answer in correct. If corrected second equation is given, i.e.

$$C(\text{graphite}) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

and if we take the above reaction in consideration then $x = y + z$ will be the answer as :

(ii) $C(\text{graphite}) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$,

$\Delta_r H° = y$ kJ/mol

(iii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$,

$\Delta_r H° = z$ kJ/mol

Summing up both the equation you will get equation (i)

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$, $\Delta_r H° = x$ kJ/mol

Hence, x, y and z are related as:

$$x = y + z$$

43 The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is

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$-3263.9\ kJ\ mol^{-1}$ at 25° C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be ($R = 8.314\ JK^{-1}\ mol^{-1}$)

[JEE Main 2018]

(a) 4152.6 (b) −452.46
(c) 3260 (d) −3267.6

Ans. ***(d)***

Key Idea Calculate the heat of combustion with the help of following formula

$$\Delta H_p = \Delta U + \Delta n_g RT$$

where, ΔH_p = Heat of combustion at constant pressure

ΔU = Heat at constant volume (It is also called ΔE)

Δn_g = Change in number of moles (In gaseous state).

R = Gas constant; T = Temperature.

From the equation,

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

Change in the number of gaseous moles i.e.

$$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2} \text{ or } -1.5$$

Now we have Δn_g and other values given in the question are

$\Delta U = -3263.9\ kJ/mol$

$T = 25°\ C = 273 + 25 = 298\ K$

$R = 8.314\ JK^{-1}mol^{-1}$

So, $\Delta H_p = (-3263.9) + (-1.5) \times 8.314 \times 10^{-3} \times 298$

$= -3267.6\ kJ\ mol^{-1}$

44 Given,

$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g); \quad \Delta_r H° = -393.5\ kJ\ mol^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta_r H° = -285.8\ kJ\ mol^{-1}$$

$$CO_2(g) + 2\ H_2O(l) \longrightarrow CH_4(g) + 2O_2(g); \quad \Delta_r H° = +890.3\ kJ\ mol^{-1}$$

Based on the above thermochemical equations, the value of $\Delta_r H°$ at 298 K for the reaction, **[JEE Main 2017]**

$$C_{(graphite)} + 2\ H_2(g) \longrightarrow CH_4(g)$$

will be

(a) + 78.8 kJ mol^{-1}
(b) + 144.0 kJ mol^{-1}
(c) − 74.8 kJ mol^{-1}
(d) − 144.0 kJ mol^{-1}

Ans. ***(c)***

Based on given $\Delta_r H°$

$$\Delta_f H° = H°_{CO_2} = -393.5\ kJ\ mol^{-1} \quad ...(i)$$

$$\Delta_f H° = H°_{H_2O} = -285.8\ kJ\ mol^{-1} \quad ...(ii)$$

$$\Delta_f H° = H°_{O_2} = 0.00 \text{ (elements)} \quad ...(iii)$$

Required thermal reaction is for $\Delta_f H°$ of CH_4

Thus, from III

$$890.3 = [\Delta_f H°(CH_4) + 2\Delta_f H°(O_2)] - [\Delta_f H°(CO_2) + 2\Delta_f H°(H_2O)]$$

$$= \Delta_f H°(CH_4) + 0] - [-393.5 - 2 \times 285.5]$$

$\therefore\ \Delta_f H°(CH_4) = -74.8\ kJ/mol$

45 The heats of combustion of carbon and carbon monoxide are −393.5 and −283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is

[JEE Main 2016]

(a) 676.5 (b) −676.5 (c) −110.5 (d) 110.5

Ans. ***(c)***

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -393.5\ kJ\ mol^{-1} \quad ...(i)$$

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2(g); \quad \Delta H = -283.5\ kJ\ mol^{-1} \quad ...(ii)$$

On subtracting Eq. (ii) from Eq. (i), we get

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta H = (-393.5 + 283.5)\ kJ\ mol^{-1} = -110\ kJ\ mol^{-1} \text{ (approx.)}$$

46 For the complete combustion of ethanol,

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

the amount of heat produced as measured in bomb calorimeter is 1364.47 kJ mol^{-1} at 25° C. Assuming ideality, the enthalpy of combustion, $\Delta_C H$ for the reaction will be

[$R = 8.314\ JK^{-1}mol^{-1}$]

[JEE Main 2014]

(a) −1366.95 kJ mol^{-1}
(b) −1361.95 kJ mol^{-1}
(c) −1460.50 kJ mol^{-1}
(d) −1350.50 kJ mol^{-1}

Ans. ***(a)***

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

Amount of heat produced in bomb calorimeter,

$\Delta u = -1364.47\ kJ mol^{-1}$

Enthalpy of a combustion reaction is

$\Delta H = \Delta u + \Delta n_g RT$

where, Δu = internal energy

Δn_g = moles of gas (products − reactants)

ΔR = Gas constant,

T = Temperature in K

As per equation,

$\Delta n_g = 2 - 3 = -1$

$T = 25°\ C = 25 + 273\ K \Rightarrow T = 298\ K$

Thus, $\Delta H = -1364.47 + \left[\frac{(-1) \times 8.314 \times 298}{1000}\right]$

$\Delta H = -1364.47 - 2.477 = -1366.947\ kJ mol^{-1}$

Hence, the enthalpy of combustion, $\Delta_c H$ for the given reaction will be $-1366.947\ kJ mol^{-1}$.

47 The value of enthalpy change (ΔH) for the reaction

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

at 27°C is $-1366.5\ kJ\ mol^{-1}$. The value of internal energy change for the above reaction at this temperature will be **[AIEEE 2011]**

(a) − 1371.5 kJ (b) − 1369.0 kJ
(c) − 1364.0 kJ (d) − 1361.5 kJ

Ans. ***(c)***

Relation between ΔH (enthalpy change) and ΔE (internal energy change) is

$$\Delta H = \Delta E + \Delta n_g RT$$

where, Δn_g = (moles of gaseous products) − (moles of gaseous reactants)

For the given reaction,

$\Delta n_g = 2 - 3 = -1$

$\Rightarrow \quad -1366.5 = \Delta E - 1 \times 8.314 \times 10^{-3} \times 300$

$\therefore \quad \Delta E = -1364.0\ kJ\ mol^{-1}$

48 Consider the reaction,

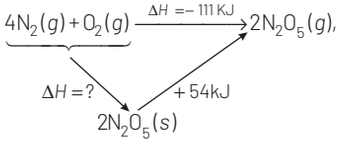
$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$, $\Delta_r H = -111\ kJ$.

If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be

(Given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1}) **[AIEEE 2011]**

(a) − 165 kJ (b) + 54 kJ
(c) + 219 kJ (d) − 219 kJ

Ans. ***(a)***



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From Hess law,

$\Delta H_f + \Delta H_{sub} = \Delta H_{reaction}$;

$\Delta H_f = \Delta H_{reaction} - \Delta H_{sub}$

$= -111\,kJ - (54\,kJ)$

$= -111 - 54\,kJ = -165\,kJ$

Thus, the enthalpy of formation, ΔH_f for $N_2O_5\,(s)$ is $-165\,kJ$.

49 The standard enthalpy of formation of NH_3 is $-46.0\ kJ\ mol^{-1}$. If the enthalpy of formation of H_2 from its atoms is $-436\ kJ\ mol^{-1}$ and that of N_2 is $-712\ kJ\ mol^{-1}$, the average bond enthalpy of N—H bond in NH_3 is **[AIEEE 2010]**

(a) $-964\ kJ\ mol^{-1}$ (b) $+352\ kJ\ mol^{-1}$

(c) $+1056\ kJ\ mol^{-1}$ (d) $-1102\ kJ\ mol^{-1}$

Ans. ***(b)***

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g),\quad \Delta_r H = -46\,kJ\,mol^{-1}$$

Bond enthalpy of $H_2 = 436\,kJ\,mol^{-1}$

[+ ve sign is taken because energy is supplied to break the H—H bond into its atoms]

Similarly, bond enthalpy of $N_2 = +712\,kJ\,mol^{-1}$

$$\Delta_r H = \left[\frac{1}{2}BE(N_2) + \frac{3}{2}BE(H_2)\right] - 3\,BE(N\text{—}H)$$

$$-46 = \left[\frac{1}{2}\times 712 + \frac{3}{2}\times 436\right] - 3\,BE(N\text{—}H)$$

$$-46 = (356 + 654) - 3\,BE(N\text{—}H)$$

$$3\,BE(N\text{—}H) = (1010) + 46$$

$$3\,BE(N\text{—}H) = 1056$$

$$BE(N\text{—}H) = 1056/3 = 352\,kJ\,mol^{-1}$$

50 On the basis of the following thermochemical data

$[\Delta_f G°H^+(aq) = 0]$

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq);\quad \Delta H = 57.32\ kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\quad \Delta H = -286.02\ kJ$$

The value of enthalpy of formation of OH^- ion at 25°C is **[AIEEE 2009]**

(a) -22.88 kJ (b) -228.88 kJ

(c) +228.88 kJ (d) -343.52 kJ

Ans. ***(b)***

Consider the heat of formation of H_2O.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\quad \Delta H = -286.20\ kJ$$

$$\Delta H_r = \Delta H_f(H_2O, l) - \Delta H_f(H_2, g) - \frac{1}{2}\Delta H_f(O_2, g)$$

$$= -286.20 = \Delta H_f(H_2O, l) - 0 - 0$$

$$\Delta H_f(H_2O, l) = -286.20$$

Now, consider the ionization of H_2O

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq),\quad \Delta H = 57.32\ kJ$$

$$\Delta H_r = \Delta H_f(H^+, aq) + \Delta H_f(OH^-, aq) - \Delta H_f(H_2O, l)$$

$$57.32 = 0 + \Delta H_f(OH^-, aq) - (-286.20)$$

Thus, $\Delta H_f(OH^-, aq) = 57.32 - 286.20 = -228.80\ kJ$.

51 Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below

$$\frac{1}{2}Cl_2\,(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^\ominus} Cl\,(g) \xrightarrow{\Delta_{EA}H^\ominus} Cl^-\,(g) \xrightarrow{\Delta_{hyd}H^\ominus} Cl^-\,(aq)$$

The energy involved in the conversion of $\frac{1}{2}Cl_2\,(g)$ to $Cl^-(aq)$ (using the data, $\Delta_{diss}H^\ominus_{Cl_2} = 240\ kJ\,mol^{-1}$

$\Delta_{EA}H^\ominus_{Cl} = -349\ kJ\,mol^{-1}$,

$\Delta_{hyd}H^\ominus_{Cl} = -381\ kJ\,mol^{-1}$) will be **[AIEEE 2008]**

(a) $+152\ kJ\,mol^{-1}$

(b) $-610\ kJ\,mol^{-1}$

(c) $-850\ kJ\,mol^{-1}$

(d) $+120\ kJ\,mol^{-1}$

Ans. ***(b)***

$$\frac{1}{2}Cl_2(g) \longrightarrow Cl^-(aq)$$

$$\Delta H = \frac{1}{2}\Delta H_{diss}(Cl_2) + \Delta H_{EA}\,Cl + \Delta H_{hyd}(Cl^-)$$

$$= \frac{240}{2} - 349 - 381 = -610\ kJ\,mol^{-1}$$

52 Assuming that water vapour is an ideal gas, the internal energy change (ΔE) when 1 mole of water is vaporised at 1 bar pressure and 100°C, (Given : molar enthalpy of vaporisation of water at 1 bar and 373 K = $41\,kJ\,mol^{-1}$ and $R = 8.3\ J\,mol^{-1}\,K^{-1}$) will be **[AIEEE 2007]**

(a) $4.100\ kJ\,mol^{-1}$ (b) $3.7904\ kJ\,mol^{-1}$

(c) $37.904\ kJ\,mol^{-1}$ (d) $41.00\ kJ\,mol^{-1}$

Ans. ***(c)***

$$H_2O(l) \longrightarrow H_2O(g)$$

$$\Delta n_g = 1 - 0 = 1$$

$$\Delta E = \Delta H - \Delta n_g RT$$

$$= 41 - (1\times 8.3\times 373\times 10^{-3}) \quad [R = 8.3\times 10^{-3}]$$

$$= 37.9\ kJ\,mol^{-1}$$

53 $(\Delta H - \Delta E)$ for the formation of carbon monoxide (CO) from its elements at 298 K is $(R = 8.314\ JK^{-1}\,mol^{-1})$ **[AIEEE 2006]**

(a) $-1238.78\ J\,mol^{-1}$

(b) $1238.78\ J\,mol^{-1}$

(c) $-2477.57\ J\,mol^{-1}$

(d) $2477.57\ J\,mol^{-1}$

Ans. ***(b)***

Calculate $\Delta H - \Delta E$ by using the formula,

$$\Delta H - \Delta E = \Delta n_g RT$$

$$= \frac{1}{2}\times 8.314\times 298 = 1238.78\ J\,mol^{-1}$$

$$\left[C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g),\quad \Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}\right]$$

54 The enthalpy changes for the following processes are listed below

$Cl_2(g) = 2Cl(g)$, $242.3\ kJ\,mol^{-1}$

$I_2\,(g) = 2I\,(g)$, $151.0\ kJ\,mol^{-1}$

$ICl(g) = I(g) + Cl(g)$, $211.3\ kJ\,mol^{-1}$

$I_2(s) = I_2(g)$, $62.76\ kJ\,mol^{-1}$

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation of ICl is **[AIEEE 2006]**

(a) $-14.6\ kJ\,mol^{-1}$

(b) $-16.8\ kJ\,mol^{-1}$

(c) $+16.8\ kJ\,mol^{-1}$

(d) $+244.8\ kJ\,mol^{-1}$

Ans. ***(c)***

$$\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow ICl(g)$$

$$\Delta H = \left[\frac{1}{2}\Delta H_{s\to g} + \frac{1}{2}\Delta H_{diss}(Cl_2) + \frac{1}{2}\Delta H_{diss}(I_2)\right] - \Delta H_{ICl}$$

$$= \left(\frac{1}{2}\times 62.76 + \frac{1}{2}\times 242.3 + \frac{1}{2}\times 151.0\right) - 211.3$$

$$= 228.03 - 211.3$$

$$\Delta H = 16.73\ kJ\,mol^{-1}$$

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55 The standard enthalpy of formation (ΔH_f°) at 298 K for methane, $CH_4(g)$ is – 74.8 kJ mol^{-1}. The addition information required to determine the average energy for C—H bond formation would be **[AIEEE 2006]**

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(b) latent heat of vaporisation of methane
(c) the first four ionisation energies of carbon and electron gain enthalpy of hydrogen
(d) the dissociation energy of hydrogen molecule, H_2

Ans. ***(a)***

Carbon is found in solid state. The state of substance affects the enthalpy change.

$C(s) \longrightarrow C(g)$ sublimation,

and $H_2(g) \longrightarrow 2H(g)$ dissociation are required for C—H bond.

56 Consider the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔE are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? **[AIEEE 2005]**

(a) $\Delta H > \Delta E$ (b) $\Delta H < \Delta E$
(c) $\Delta H = \Delta E$ (d) $\Delta H = 0$

Ans. ***(b)***

According to relationship of ΔH and ΔE,

$\Delta H = \Delta E + \Delta n_g RT$

ΔH = enthalpy change (at constant pressure)

ΔE = internal energy change (at constant volume)

(given reaction is exothermic)

(Δn_g = moles of gaseous products – moles of gaseous reactants)

For the reaction

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$\Delta n_g = 2 - 4 = -2$

Thus, $\Delta H = \Delta E - 2RT$

$\Rightarrow \quad \Delta H < \Delta E$

Note Numerical value of $\Delta H < \Delta E$ in exothermic reaction and when $\Delta n_g < 0$.

57 If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is – 200 kJ mol^{-1}. The bond dissociation energy of X_2 will be **[AIEEE 2005]**

(a) 400 kJ mol^{-1} (b) 300 kJ mol^{-1}
(c) 200 kJ mol^{-1} (d) None of these

Ans. ***(d)***

Formation of XY is shown as

$$X_2 + Y_2 \longrightarrow 2XY$$

$$\Delta H = [(BE)_{X—X} + (BE)_{Y—Y}] - [2(BE)_{X—Y}]$$

If (BE) of $X—Y = a$ KJ/mol

then, (BE) of $(X—X) = a$ and (BE) of

$$(Y—Y) = \frac{a}{2} \qquad \left[\because \frac{1}{2}X_2 + \frac{1}{2}Y_2 \rightarrow XY\right]$$

$$\therefore \qquad \Delta H_f\,(X—Y) = -200 \text{ kJ}$$

$$\therefore -400 (\text{for 2 mol } XY) = \left(a + \frac{a}{2} - 2a\right)$$

$$-400 = -\frac{a}{2};\ a = +800 \text{ kJ}$$

The bond dissociation energy of $X_2 = 800$ kJ mol^{-1}.

58 The enthalpies of combustion of carbon and carbon monoxide are – 393.5 and – 283 kJ mol^{-1}, respectively. The enthalpy of formation of carbon monoxide per mole is **[AIEEE 2004]**

(a) 110.5 kJ (b) 676.5 kJ
(c) – 676.5 kJ (d) – 110.5 kJ

Ans. ***(d)***

I $C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -393.5$ kJ

II $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -283.0$ kJ

[I - II] gives

III $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$,

$[\Delta H = -393.5 + 283.0$ kJ$]$ $\Delta H = -110.5$ kJ

The equation III also represents formation of one mole of CO and thus, enthalpy change is the heat of formation of $CO(g)$.

59 The enthalpy change for a reaction does not depend upon the **[AIEEE 2003]**

(a) physical state of reactants and products
(b) use of different reactants for the same product
(c) nature of intermediate reaction steps
(d) difference in initial or final temperatures of involved substances

Ans. ***(c)***

Enthalpy change is state function and depends only on initial and final condition do not depend on path or nature of its intermediates.

60 If at 298 K, the bond energies of C—H, C—C, C$\equiv$C and H—H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction, $H_2C{=}CH_2(g) + H_2(g) \longrightarrow H_3C{—}CH_3(g)$ at 298 K will be **[AIEEE 2003]**

(a) + 250 kJ (b) – 250 kJ
(c) + 125 kJ (d) – 125 kJ

Ans. ***(d)***

$CH_2{=}CH_2 + H_2 \longrightarrow CH_3{—}CH_3$

$\Delta H = (BE)_{\text{reactants}} - (BE)_{\text{products}}$

$= 4(BE)_{C-H} + (BE)_{C=C} + (BE)_{H—H} - [6(BE)_{C—H} + (BE)_{C—H}]$

$= -125$ kJ

TOPIC 3

Entropy, Free Energy Change and Spontaneity

61 For the reaction, $2NO_2(g) \rightleftharpoons N_2O_4(g)$, when $\Delta S = -176.0\,JK^{-1}$ and $\Delta H = -57.8$ kJ mol^{-1}, the magnitude of ΔG at 298 K for the reaction is ..... kJ mol^{-1}. (Nearest integer) **[2021, 1 Sep Shift-II]**

Ans. ***(5)***

Given, $\Delta H = -57.8$ kJ mol^{-1}

$\Delta S = -176\,JK^{-1}\,mol^{-1}$

$T = 298$ K

Using Gibb's free energy relation

$$\Delta G = \Delta H - T\Delta S$$

where, ΔG = change in Gibb's free energy

ΔH = change in enthalpy

T = temperature

ΔS = change in entropy

$\Delta G = 57.8$ kJ / mol – [298 K $\times (-176\,JK^{-1}mol^{-1})$]

$$= 57.8 \text{ kJ/mol} - \left(298 \times \frac{-176}{1000} \text{ kJ}\right)$$

$[\therefore 1\text{kJ} = 1000\text{ J}]$

$= -5.352$ kJ / mol

$|\Delta G| = 5.352$

Hence, answer is 5.

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62 The incorrect expression among the following is **[2021, 31 Aug Shift-II]**

(a) $\frac{\Delta G_{System}}{\Delta S_{Total}} = -T$ (at constant p)

(b) $\ln k = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$

(c) $k = e^{-\frac{\Delta G^\circ}{RT}}$

(d) For isothermal process,
$W_{reversible} = -nRT \ln \frac{V_f}{V_i}$

Ans. ***(b)***

All the expression of thermodynamics are correct except
$$\ln k = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$$
As we know,
$$\Delta G = \Delta H - T\Delta S^\circ \quad ...(i)$$
Also $\Delta G = -RT \ln K$ ...(ii)
$\therefore$ From (i) and (ii)
$$-RT \ln K = \Delta H - T\Delta S^\circ$$
$$\therefore \quad \ln K = \frac{-\Delta H}{RT} + \frac{\Delta S^\circ}{R}$$
The corect expression is
$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$$

63 Data given for the following reaction is as follows.

$FeO(s) + C_{(graphite)} \longrightarrow Fe(s) + CO(g)$

Substance	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
$FeO(s)$	−266.3	57.49
$C_{(graphite)}$	0	5.74
$Fe(s)$	0	27.28
$CO(g)$	−110.5	197.6

The minimum temperature in K at which the reaction becomes spontaneous is ..... (Integer answer) **[2021, 27 Aug Shift-II]**

Ans. ***(964)***

$FeO(s) + C_{graphite} \longrightarrow Fe(s) + CO(g)$

$\Delta H^\circ_{reaction} = \Delta H^\circ_{f\,(product)} - \Delta H^\circ_{f\,(reactants)}$

$= [\Delta H^\circ_{f\,(Fe)} + \Delta H^\circ_{f\,(CO)}] - [\Delta H^\circ_{f\,(FeO)} - \Delta H^\circ_{f\,(C)}]$

$= [0 + (-110.5)] - [-266.3 - 0]$

$= 156\,kJ^{-1}\ mol^{-1}$

$\Delta S^\circ_{reaction} = \Delta S^\circ_{product} - \Delta S^\circ_{reactant}$

$= [\Delta S^\circ_{(Fe)} + \Delta S^\circ_{(CO)}] - [\Delta S^\circ_{(FeO)} - \Delta S^\circ_{(C)}]$

$= [27.28 + 197.6] - [57.49 + 5.79]$

$= 161\ J\ K^{-1}\ mol^{-1}$

According to Gibb's equation,
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

The reaction becomes spontaneous when ΔG° is atleast zero or negative.

$0 = \Delta H^\circ - T\Delta S^\circ$

$T\Delta S^\circ = \Delta H^\circ$

$\Rightarrow T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{156\,kJ\ mol^{-1}}{161\ J\ K^{-1}\ mol^{-1}}$

$= \frac{156000\ mol^{-1}}{161\ J\ K^{-1}\ mol^{-1}} = 964\,K$

The temperature at which reaction becomes spontaneous is 964 K.

64 For a given chemical reaction, $A \longrightarrow B$ at 300 K the free energy change is −49.4 kJ mol^{-1} and the enthalpy of reaction is 51.4 kJ mol^{-1}. The entropy change of the reaction is ..... JK^{-1}mol^{-1}. **[2021, 20 July Shift-II]**

Ans. ***(360)***

For the reaction, $A \xrightarrow{300K} B$

Gibb's free energy change

Given, $\Delta G = -49.4$ kJ/mol

Change in enthalpy

$\Delta H_{reaction} = 51.4$ kJ/mol

Change in entropy $\Delta S_{reaction} = ?$

According to Gibbs free energy,

$\Delta G = \Delta H - T\Delta S$

$\Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T}$

$= \frac{51.4 - (-49.4)}{300} \times 1000 \frac{J}{mol\ K}$

$\Delta S_{reaction} = 336$ J/mol K

65 During which of the following processes, does entropy decrease?

A. Freezing of water to ice at 0°C.

B. Freezing of water to ice at −10°C.

C. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

D. Adsorption of $CO(g)$ and lead surface.

E Dissolution of NaCl in water. **[2021, 17 March Shift-II]**

(a) A, B, C and D (b) B and C

(c) A and E (d) A, C and E

Ans. ***(a)***

Entropy will decrease in A,B,C and D processes.

A, B → Freezing of water will decrease entropy as particles will move closer and forces of attraction will increase. This leads to a decrease in randomness. So, entropy decreases.

(A) Water $\xrightarrow{0°C}$ ice; $\Delta S = -ve$

(B) Water $\xrightarrow{-10°C}$ ice; $\Delta S = -ve$

(C) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta S = -ve$

Number of moles are decreasing

$n = 2 - (3 + 1)$

$n = -2$

So, entropy decreases.

(D) Adsorption; $\Delta S = -ve$

Adsorption will lead to a decrease in the randomness of gaseous particles.

So, entropy decreases.

(E) $NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$; $\Delta S > 0$

The number of species on product side is more than the number of species on reactant side. So, entropy increases on dissolution of NaCl in water.

66 For a dimerisation reaction

$2A(g) \longrightarrow A_2(g)$,

at 298 K, $\Delta U^\ominus = -20$ kJ mol^{-1}, $\Delta S^\ominus = -30$ JK^{-1} mol^{-1}, then the $\Delta G^\ominus$ will be ..... J. **[2020, 5 Sep Shift-II]**

Ans. ***(13537.57)***

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta H = -20 \times 1000 - 1 \times 8.314$ J/mol.K $\times$ 298 K

$= -22477.572$ J

$\Delta G = \Delta H - T\Delta S$

$\Delta G = -22477.572 + 298 \times 30$

$\Delta G = -13537.57$ Joule

67 For the reaction; $A(l) \longrightarrow 2B(g)$

$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K.

Hence, ΔG in kcal is ..... . **[2020, 8 Jan Shift-I]**

Ans. ***(2.70)***

Given: $\Delta U = 2.1$ kcal

$\Delta S = 20$ cal K^{-1} $= \frac{20}{1000}$ kcal K^{-1}

$A(l) \rightleftharpoons 2B(g)$

$\therefore \quad \Delta n_g = 2$ mol

$R = 2$ cal K^{-1} mol^{-1}

$= \frac{2}{1000}$ kcal K^{-1} mol^{-1}

As we know,

$\Delta G = \Delta H - T\Delta S$

and $\Delta H = \Delta U + \Delta n_g RT$

$\therefore \quad \Delta G = \Delta U + \Delta n_g RT - T\Delta S$

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$$\therefore\ \Delta G = 2.1 + \frac{2\times2\times300}{1000} - \frac{300\times20}{1000}$$
$$= 2.1 + 1.2 - 6 = -2.70$$

68 The true statement amongst the following is **[2020, 9 Jan Shift-II]**

(a) S is not a function of temperature but ΔS is a function of temperature.
(b) Both ΔS and S are functions of temperature.
(c) Both S and ΔS are not functions of temperature.
(d) S is a function of temperature but ΔS is not a function of temperature.

Ans. ***(b)***

Statement (b) is a true statement whereas all other statements are incorrect.

By definition,

$$dS = \frac{dQ}{T} \text{ and } \Delta S = \frac{\int dQ}{T}$$

$\therefore \Delta S$ is a function of temperature : S is also a function of temperature.

69 A process will be spontaneous at all temperature if **[2019, 10 April Shift-I]**

(a) $\Delta H > 0$ and $\Delta S < 0$
(b) $\Delta H < 0$ and $\Delta S > 0$
(c) $\Delta H < 0$ and $\Delta S < 0$
(d) $\Delta H > 0$ and $\Delta S > 0$

Ans. ***(b)***

A process will be spontaneous when its free energy (Gibb's energy) change will be negative, i.e. $\Delta G < 0$.

Spontaneity of a process is decided by the value of ΔG, which can be predicted from the Gibb's equation, $\Delta G = \Delta H - T\Delta S$ for positive/negative signs of ΔH and ΔS at any/higher/lower temperature as:

ΔH	ΔS	Comment on temperature (T)	ΔG	Comment on the process
<0	>0	at any temp.	<0	spontaneous
>0	<0	at any temp.	>0	non-spontaneous
<0	<0	at lower temp.	<0	spontaneous
>0	>0	at higher temp.	<0	spontaneous

70 The incorrect match in the following is **[2019, 12 April Shift-II]**

(a) $\Delta G^\circ < 0, K > 1$ (b) $\Delta G^\circ = 0, K = 1$
(c) $\Delta G^\circ > 0, K < 1$ (d) $\Delta G^\circ < 0, K < 1$

Ans. ***(d)***

The incorrect match is $\Delta G^\circ < 0, K < 1$.

For an ideal gas $\Delta G^\circ = -RT\ln K$.

$$\therefore \quad \ln K = -\frac{\Delta G^\circ}{RT} \text{ and } K = e^{-\Delta G^\circ/RT}$$

The above equation is helpful in predicting the spontaneity of the reaction. e.g.

(i) If $\Delta G^\circ < 0$, $-\Delta G^\circ/RT = +$ ve and $e^{-\Delta G^\circ/RT} > 1$ and hence, $K > 1$. It means that the reaction occur spontaneously in the forward direction or products predominate over reactants.

(ii) If $\Delta G^\circ > 0$; $-\Delta G^\circ/RT = -$ ve and $e^{-\Delta G^\circ/RT} < 1$ and hence, $K < 1$. It means that the reaction is non-spontaneous in forward direction (i.e. product side) but spontaneous in reverse direction (i.e. reactants predominate over products or the reaction occurs rarely).

(iii) When $K = 1$, then $\Delta G^\circ = 0$. This situation generally occur at equilibrium.

71 The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is (Specific heat of water liquid and water vapour are 4.2 $kJK^{-1}kg^{-1}$ and 2.0$kJK^{-1}kg^{-1}$; heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491kJkg^{-1} respectively). (log273 = 2.436, log373 = 2.572, log383 = 2.583)

(a) 9.26 kJ kg^{-1} K^{-1} (b) 8.49 kJ $kg^{-1}K^{-1}$
(c) 7.90 kJ $kg^{-1}K^{-1}$ (d) 2.64 kJ $kg^{-1}K^{-1}$

[2019, 9 Jan Shift-II]

Ans. ***(a)***

The conversion of 1 kg of ice at 273 K into water vapours at 383 K takes place as follows:

$$H_2O(s)\ (273K) \xrightarrow{\Delta S_1} H_2O(l)\ (273K) \xrightarrow{\Delta S_2} H_2O(l)\ (373K)$$
$$\downarrow \Delta S_3$$
$$H_2O(g)\ (383K) \xleftarrow{\Delta S_4} H_2O(g)\ (373K)$$

$$\Delta S_1 = \frac{\Delta H_{Fusion}}{\Delta T_{Fusion}} = \frac{334\text{ kJ kg}^{-1}}{273\text{ K}}$$
$$= 1.22\text{ kJ kg}^{-1}\text{ K}^{-1}$$
$$\Delta S_2 = C\ln\frac{T_2}{T_1} = 4.2\text{ kJ K}^{-1}\text{kg}^{-1}\ln\left(\frac{373\text{ K}}{273\text{ K}}\right)$$
$$= 4.2\times2.303(\log373 - \log273)\text{ kJ K}^{-1}\text{kg}^{-1}$$
$$= 4.2\times2.303(2.572 - 2.436)$$
$$= 1.31\text{ kJ K}^{-1}\text{kg}^{-1}$$
$$\Delta S_3 = \frac{\Delta H_{vap.}}{\Delta T_{vap.}} = \frac{2491\text{ kJ kg}^{-1}}{373\text{ K}}$$
$$= 6.67\text{ kJ kg}^{-1}\text{K}^{-1}$$
$$\Delta S_4 = C\ln\frac{T_2}{T_1} = 2\text{ kJ K}^{-1}\text{kg}^{-1}\ln\left(\frac{383\text{ K}}{373\text{ K}}\right)$$
$$= 2\times2.303(\log383 - \log373)\text{ kJ K}^{-1}\text{ kg}^{-1}$$
$$= 2\times2.303(2.583 - 2.572)\text{ kJ K}^{-1}\text{ kg}^{-1}$$
$$= 0.05\text{ kJ K}^{-1}\text{ kg}^{-1}$$
$$\Delta S_{Total} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$
$$= 1.22 + 1.31 + 6.67 + 0.05$$
$$= 9.26\text{kJ kg}^{-1}\text{ K}^{-1}$$

72 A process has $\Delta H = 200\text{ J mol}^{-1}$ and $\Delta S = 40\text{ JK}^{-1}\text{ mol}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous

(a) 20 K (b) 4 K (c) 5 K (d) 12 K

[2019, 10 Jan Shift-II]

Ans. ***(c)***

$$\Delta G = \Delta H - T\Delta S$$

The process will be spontaneous, when $\Delta G = -$ ve, i.e. $|T\Delta S| > |\Delta H|$

Given : $\Delta H = 200\text{ J mol}^{-1}$

and $\Delta S = 40\text{ JK}^{-1}\text{ mol}^{-1}$

$$\Rightarrow \quad T > \frac{|\Delta H|}{|\Delta S|} = \frac{200}{40} = 5\text{ K}$$

So, the minimum temperature for spontaneity of the process is 5 K.

73 The process with negative entropy change is

(a) synthesis of ammonia from N_2 and H_2
(b) dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$
(c) dissolution of iodine in water
(d) sublimation of dry ice

[2019, 10 Jan Shift-II]

Ans. ***(a)***

The explanation of all the options are as follows :

(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, $\Delta n_g = 2 - (1+3) = -2$
So, ΔS is also negative (entropy decreases)

(b) $CaSO_4(s) \xrightarrow{\Delta} CaO(s) + SO_3(g)$, $\Delta n_g = (1+0) - 0 = +1$
So, $\Delta S = +$ ve

(c) In dissolution, $\Delta S = +$ ve because molecules/ions of the solid solute (here, iodine) become free to move

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in solvated/dissolved state of the solution,

$$I_2(s) \xrightarrow[(KI)]{\text{Water}} I_2(aq)$$

(d) In sublimation process, molecules of solid becomes quite free when they become gas,

$$\underset{\text{Dry ice}}{CO_2(s)} \longrightarrow CO_2(g)$$

So, ΔS will be positive.

74 For the chemical reaction, $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as

$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}) = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at T is **[2019, 11 Jan Shift-I]**

(a) Y if $T = 280$ K
(b) X if $T = 350$ K
(c) X if $T = 315$ K
(d) Y if $T = 300$ K

Ans. ***(c)***

For a given value of T,

(i) If $\Delta_r G^\circ$ becomes < 0, the forward direction will be spontaneous and then the major and minor components will be Y and X respectively.

(ii) If $\Delta_r G^\circ$ becomes > 0, the forward direction will be non-spontaneous and then the major and minor components will be X and Y respectively.

(a) $\Delta_r G^\circ = 120 - \frac{3}{8} \times 280 = 15$

i.e. $\Delta_r G^\circ > 00$, major component $= X$;

(b) $\Delta_r G^\circ = 120 - \frac{3}{8} \times 350 = -11.25$

i.e. $\Delta_r G^\circ < 0$, major component $= Y$

(c) $\Delta_r G^\circ = 120 - \frac{3}{8} \times 315 = 1.875$

i.e. $\Delta_r G^\circ > 0$, major component $= X$

(d) $\Delta_r G^\circ = 120 - \frac{3}{8} \times 300 = 7.5$

i.e. $\Delta_r G^\circ > 0$, major component $= X$

75 Two blocks of the same metal having same mass and at temperature T_1 and T_2 respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is **[2019, 11 Jan Shift-I]**

(a) $^2C_p \ln\left[\frac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$

(b) $^2C_p \ln\left[\frac{T_1+T_2}{4T_1T_2}\right]$

(c) $C_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$

(d) $^2C_p \ln\left[\frac{T_1+T_2}{2T_1T_2}\right]$

Ans. ***(c)***

At the thermal equilibrium,

$$\text{final temperature } T_f = \frac{T_1+T_2}{2}$$

$\Rightarrow$ for the 1st block, $\Delta S_{\text{I}} = C_p \ln \frac{T_f}{T_1}$

$\Rightarrow$ for the 2nd block, $\Delta S_{\text{II}} = C_p \ln \frac{T_f}{T_2}$

When brought in contact with each other,

$$\Delta S = \Delta S_{\text{I}} + \Delta S_{\text{II}} = C_p \ln \frac{T_f}{T_1} + C_p \ln \frac{T_f}{T_2}$$

$$= C_p \ln\left(\frac{T_f}{T_1} \times \frac{T_f}{T_2}\right) = C_p \ln\left[\frac{T_f^2}{T_1T_2}\right]$$

$$= C_p \ln\left[\frac{\left(\frac{T_1+T_2}{2}\right)^2}{T_1T_2}\right] = C_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$$

76 The reaction, $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$, for which $\Delta_r H^\circ = +491.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 198.0 \text{ JK}^{-1}\text{mol}^{-1}$, is not feasible at 298 K. Temperature above which reaction will be feasible is **[2019, 11 Jan Shift-II]**

(a) 2040.5 K (b) 1890.0 K
(c) 2380.5 K (d) 2480.3 K

Ans. ***(d)***

According to Gibbs-Helmholtz equation,

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

For a reaction to be feasible (spontaneous)

$$\Delta_r G^\circ < 0$$

$$\Delta_r H^\circ - T\Delta_r S^\circ < 0$$

Given, $\Delta_r H^\circ = +491.1 \text{ kJ mol}^{-1}$,

$$\Delta_r S^\circ = 198 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\therefore \quad 491.1 \times 10^3 - T \times 198 < 0$$

$$T > \frac{491.1 \times 10^3}{198} = 2480.3 \text{ K}$$

$\therefore$ Above 2480.3 K reaction will become spontaneous.

77 The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by, $\Delta_r G^\circ = A - BT$
Where A and B are non-zero constants.
Which of the following is true about this reaction? **[2019, 11 Jan Shift-II]**

(a) Endothermic if, $A < 0$ and $B > 0$
(b) Exothermic if, $B < 0$
(c) Exothermic if, $A > 0$ and $B < 0$
(d) Endothermic if, $A > 0$

Ans. ***(d)***

According to Gibb's Helmholtz equation,

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

Given, $\Delta_r G^\circ = A - BT$

On comparing above two equations, we get,

$$A = \Delta H^\circ \text{ and } \Delta S^\circ = B$$

We know that, if ΔH° is negative, reaction is exothermic and when it is positive, reaction is endothermic.

$\therefore$ If $A > 0$, i.e. positive, reaction is endothermic.

78 The following reaction is performed at 298K

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of NO (g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K? ($K_p = 1.6 \times 10^{12}$) **[JEE Main 2015]**

(a) $R(298)\ln(1.6 \times 10^{12}) - 86600$
(b) $86600 + R(298)\ln(1.6 \times 10^{12})$
(c) $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$
(d) $0.5[2 \times 86600 - R(298)\ln(1.6 \times 10^{12})]$

Ans. ***(d)***

For the given reaction,

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Given, $\Delta G_f^\circ (NO) = 86.6 \text{ kJ / mol}$

$$\Delta G_f^\circ (NO_2) = ? \quad K_p = 1.6 \times 10^{12}$$

Now, we have,

$$\Delta G_f^\circ = 2\Delta G_{f(NO_2)}^\circ - [2\Delta G_{f(NO)}^\circ + \Delta G_{f(O_2)}^\circ]$$

$$= -RT\ln K_p = 2\Delta G_{f(NO_2)}^\circ - [2 \times 86{,}600 + 0]$$

$$\Delta G_{f(NO_2)}^\circ = \frac{1}{2}[2 \times 86{,}600 - R \times 298\ln(1.6 \times 10^{12})]$$

$$\Delta G_{f(NO_2)}^\circ = 0.5[2 \times 86{,}600 - R \times (298)\ln(1.6 \times 10^{12})]$$

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89 The incorrect expression among the following is

(a) $\frac{\Delta G_{system}}{\Delta G_{total}} = -T$ **[AIEEE 2012]**

(b) In isothermal process, $W_{reversible} = -nRT \ln \frac{V_f}{V_i}$

(c) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$

(d) $K = e^{-\Delta G^\circ / RT}$

Ans. ***(c)***

According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S$$

(a) For a system, total entropy change $= \Delta S_{total}$

$$\Delta H_{total} = 0$$

$$\therefore \quad \Delta G_{system} = -T\Delta S_{total}$$

$$\therefore \quad \frac{\Delta G_{system}}{\Delta S_{total}} = -T$$

Thus, (a) is correct.

(b) For isothermal reversible process, $\Delta E = 0$

By first law of thermodynamics, $\Delta E = q + W$

$$\therefore \quad W_{reversible} = -q = -\int_{V_i}^{V_f} p\,dV$$

$$\Rightarrow \quad W_{reversible} = -nRT \ln \frac{V_f}{V_i}$$

Thus, (b) is correct.

(c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ...(i)

Also, $\Delta G^\circ = -RT \ln K$

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

$$\ln K = \frac{(\Delta H^\circ - T\Delta S^\circ)}{RT} \quad [\text{from Eq. (i)}]$$

Thus, (c) is incorrect.

(d) The standard free energy (ΔG°) is related to equilibrium constant K as

$$\Delta G^\circ = -RT \ln K$$

$$\therefore \quad \ln K = -\frac{\Delta G^\circ}{RT} \Rightarrow K = e^{-\Delta G^\circ / RT}$$

Thus, (d) is also correct.

80 The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27° C is **[AIEEE 2011]**

(a) 38.3 J mol^{-1} K^{-1} (b) 35.8 J mol^{-1} K^{-1}

(c) 32.3 J mol^{-1} K^{-1} (d) 42.3 J mol^{-1} K^{-1}

Ans. ***(a)***

Entropy change for n moles of isothermal expansion of an ideal gas from volume V_1 to volume V_2 is

$$\Delta S = 2.303\, nR \log \frac{V_2}{V_1}$$

Here, $n = 2$, $V_2 = 100\ dm^3$, $V_1 = 10\ dm^3$

$$= 2.303 \times 2 \times 8.3143 \log \frac{100}{10}$$

$$= 38.296\ J\ mol^{-1} K^{-1}$$

81 For a particular reversible reaction, at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when **[AIEEE 2010]**

(a) $T_e > T$ (b) $T > T_e$

(c) T_e is 5 times T (d) $T = T_e$

Ans. ***(b)***

$$\Delta G = \Delta H - T\Delta S$$

Here, ΔG = Gibb's free energy

ΔH = Enthalpy change

ΔS = Entropy change

T = Temperature

As equilibrium, $\Delta G = 0$. Thus, $T\Delta S = \Delta H$, as ΔH and ΔS are +ve, for a reaction to be feasible (spontaneous), ΔG should be –ve. This can be possible only when

$T\Delta S > T_e \Delta H$ *i.e.*, $T\Delta S > T_e \Delta S$

or $T > T_e$

[T_e = temperature at equilibrium]

82 In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are –166.2, –237.2 and –394.4 kJ mol^{-1}, respectively. If standard enthalpy of combustion of methanol is –726 kJ mol^{-1}, efficiency of the fuel cell will be **[AIEEE 2009]**

(a) 80% (b) 87%

(c) 90% (d) 97%

Ans. ***(d)***

Percentage efficiency of the fuel cell

$$= \frac{\Delta G}{\Delta H} \times 100$$

The concerned reaction is

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta G_r = [\Delta G_f(CO_2, g) + 2\Delta G_f(H_2O, l)] - [-\Delta G_f(CH_3OH, l) - \frac{3}{2}\Delta G_f(O_2, g)]$$

$$= -394.4 + 2(-237.2) - (-166.2) - 0$$

$$= -394.4 - 474.4 + 166.2$$

$$= -702.6\ kJ\ mol^{-1}$$

Percentage efficiency

$$= \frac{702.6}{726} \times 100 = 96.78\% \approx 97\%$$

83 Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. For the reaction, $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature will be **[AIEEE 2008]**

(a) 1250 K (b) 500 K

(c) 750 K (d) 1000 K

Ans. ***(c)***

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$$

$$\Delta S_{reaction} = S_{products} - S_{reactants}$$

$$\Delta S_{reaction} = 50 - \left(\frac{3}{2} \times 40 + \frac{1}{2} \times 60\right)$$

$$= -40\ J\ mol^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

At equilibrium as $\Delta G = 0$

$$\therefore \quad \Delta H = T\Delta S$$

$$\Rightarrow \quad T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{40} = 750\ K$$

84 Identify the correct statement regarding a spontaneous process. **[AIEEE 2007]**

(a) For a spontaneous process in an isolated system, the change in entropy is positive

(b) Endothermic processes are never spontaneous

(c) Exothermic processes are always spontaneous

(d) Lowering of energy in the reaction process is the only criteria for spontaneity

Ans. ***(a)***

In an isolated system where either mass and energy are not exchanged with surrounding for that spontaneous process, the change in entropy is positive.

85 In conversion of limestone to lime, $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ the values of ΔH° and ΔS° are + 179.1 kJ mol^{-1} and 160.2 J / K, respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not

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change with temperature, temperature above which conversion of limestone to lime will be spontaneous is **[AIEEE 2007]**

(a) 1008 K (b) 1200 K
(c) 845 K (d) 1118 K

Ans. ***(d)***

The entropy change can be given as

$$\Delta S = \frac{\Delta H}{T}$$

$$\Delta S = 160.2 \text{ J/K}$$

$$\Delta H = 179.1 \times 10^3 \text{ J/mol}$$

$$T = \frac{179.1 \times 10^3 \text{ J/mol}}{160.2 \text{ J/K}}$$

$$= 1117.97 \text{ K} \approx 1118 \text{ K}$$

86 For a spontaneous reaction, the ΔG, equilibrium constant (K) and E°_{cell} will be respectively **[AIEEE 2005]**

(a) $-$ ve, > 1, $-$ ve
(b) $-$ ve, < 1, $-$ ve
(c) $+$ ve, > 1, $-$ ve
(d) $-$ ve, > 1, $+$ ve

Ans. ***(d)***

The standard free energy related to equilibrium constant K as

$$\Delta G^\circ = -2.303\, RT \log K_{eq};$$

$$\Delta G^\circ = -nFE^\circ_{cell}$$

If a cell reaction is spontaneous (proceeding in forward side), it means

$$K_{eq} > 1$$

and $E^\circ_{cell} = +$ ve

Thus, $\Delta G^\circ = -$ ve

87 In an irreverible process taking place at constant T and p and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria **[AIEEE 2003]**

(a) $(dS)_{V,E} < 0, (dG)_{T,p} < 0$
(b) $(dS)_{V,E} > 0, (dG)_{T,p} < 0$
(c) $(dS)_{V,E} = 0, (dG)_{T,p} = 0$
(d) $(dS)_{V,E} = 0, (dG)_{T,p} > 0$

Ans. ***(b)***

An irreversible process
$\Rightarrow$ spontaneous process
$\Rightarrow (dS)_{V,E}$ (change in entropy) $= +$ ve > 0
$\Rightarrow (dG)_{T,p}$ (change in Gibbs free energy)
$-$ ve < 0

88 The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is **[AIEEE 2003]**

(a) $\Delta G = RT \ln K_c$ (b) $-\Delta G = RT \ln K_c$
(c) $\Delta G^\circ = RT \ln K_c$ (d) $-\Delta G^\circ = RT \ln K_c$

Ans. ***(d)***

Relationship between free energy and equilibrium constant,

$$-\Delta G^\circ = RT \ln K_c$$

89 A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water, then **[AIEEE 2002]**

	ΔH	ΔS
(a)	+ ve	+ ve
(b)	– ve	– ve
(c)	– ve	+ ve
(d)	+ ve	– ve

Ans. ***(a)***

For spontaneity, $\Delta G = -$ ve

$$\Delta G = \Delta H - T\Delta S$$

ΔH, for endothermic process + ve
At lower temperature, ΔS + ve
Hence, $\Delta G = +$ ve
But at high temperature, $T\Delta S$ will be greater than ΔH.
Hence, $\Delta G = -$ve, spontaneous.

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06
Solutions

TOPIC 1
Expression of Concentration

01 If 80 g of copper sulphate $CuSO_4 \cdot 5H_2O$. is dissolved in deionised water to make 5 L of solution. The concentration of the copper sulphate solution is $x \times 10^{-3}$ mol L^{-1}. The value of x is ..... .
[Atomic masses Cu = 63.54 u, S = 32 u, O = 16 u, H = 1 u]
[2021, 1 Sep Shift-II]

Ans. ***(64)***

Given, mass of $CuSO_4.5H_2O = 80$ g

The concentration of copper sulphate solution is $x \times 10^{-3}$ mol/L.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}} \quad ...(i)$$

Molar mass of $CuSO_4 \cdot 5H_2O = 63.54 + 32 + 16 \times 4$
$= 5 \times 18 = 249.54$ g / mol

$$\text{Number of moles of solute} = \frac{\text{Weight of solute}}{\text{Molecular mass of solute}}$$
$$= \frac{80 \text{ g}}{249.54 \text{ g / mol}} = 0.32 \text{ mol}$$

Volume of solution = 5 L

From Eq. (i),

$$\text{Molarity} = \frac{0.3205}{5} = 64.11 \times 10^{-3} \text{ mol / L}$$

$\therefore \quad x = 64.11$

or $\quad x \approx 64$

Hence, answer is 64.

02 The molarity of the solution prepared by dissolving 6.3 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in 250 mL of water in mol L^{-1} is $x \times 10^{-2}$. The value of x is ..... (Nearest integer)
[Atomic mass H = 1.0, C = 12.0, O = 16.0]
[2021, 31 Aug Shift-I]

Ans. ***(20)***

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution (in litre)}}$$
$$= \frac{\text{weight of solute/molecular mass of solute}}{\text{volume of solution (in litre)}}$$

Molecular mass of solute $[H_2C_2O_4 \cdot 2H_2O] = 126$ g

$$x \times 10^{-2} = \frac{6.3 \text{ g} / 126 \text{ g}}{250 \text{ mL}} \times 1000$$
$$x \times 10^{-2} = 0.2$$
$$x \times 10^{-2} = 20 \times 10^{-2}$$
$\therefore \quad x = 20$

03 The density of NaOH solution is 1.2 g cm^{-3}. The molality of this solution is ..... m.
(Round off to the nearest integer)
[Use : Atomic masses : Na = 23.0 u, O = 16.0 u, H = 1.0 u, density of H_2O : 1.0 g cm^{-3}]
[2021, 27 July Shift-I]

Ans. ***(5)***

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight of solution (kg)}}$$

Consider 1 litre solution, (1 litre = 1000 g)

Density of water is 1 g/mL

Mass of solution = Density × Volume
$= 1.2 \times 1000$ g
$= 1200$ g

Neglecting volume of NaOH.

Mass of water = 1000 g

Mass of NaOH = (1200 – 1000) g
= 200 g

$$\text{Moles of NaOH} = \frac{200}{40} = 5 \text{ mol}$$

$$\text{Molarity} = \frac{5 \text{ mol}}{1 \text{ kg}} = 5 \text{ mol/kg}$$

04 100 mL of Na_3PO_4 solution contains 3.45 g of sodium. The molarity of the solution is ..... $\times 10^{-2}$ mol L^{-1}. (Nearest integer)
[Atomic masses - Na = 23.0 u, O = 16.0 u, P = 31.0 u]
[2021, 26 Aug Shift-II]

Ans. ***(50)***

$$\text{Number of mole of } Na^+ \text{ ions} = \frac{\text{mass of sodium}}{\text{molar mass of sodium}}$$
$$= \frac{3.45}{23}$$

So, number of mole of Na_3PO_4
$$= \frac{\text{moles of sodium}}{3}$$
{as 1 molecule of Na_3PO_4 contains 3 atoms of Na}
$$= \frac{3.45}{3 \times 23} = 0.05$$

$$\text{Molarity} = \frac{\text{Moles of } Na_3PO_4}{\text{Volume of solution (in L)}}$$
$$= \frac{0.05}{100} \times 1000$$
$$= 0.50$$
$$= 50 \times 10^{-2}$$

$\therefore$ Answer is 50.

05 The exact volumes of 1 M NaOH solution required to neutralise 50 mL of 1 M H_3PO_3 solution and 100 mL of 2 M H_3PO_2 solution, respectively, are
[2021, 16 March Shift-II]

(a) 100 mL and 100 mL
(b) 100 mL and 50 mL
(c) 100 mL and 200 mL
(d) 50 mL and 50 mL

Ans. ***(c)***

$$\underset{\substack{50 \text{ mL} \\ 1\text{M}}}{H_3PO_3} + 2\underset{\substack{1\text{M} \\ V=?}}{NaOH} \longrightarrow Na_2HPO_3 + 2H_2O$$

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Millimoles of $H_3PO_3 = M \times V = 1 \times 50 = 50$

For 1 millimole of H_3PO_3, we require 2 millimoles of NaOH.

For 50 millimole of H_3PO_3, we require $(2 \times 50) = 100$ millimoles of NaOH.

Millimoles of NaOH $= M \times V = 100$

$1 \times V = 100$

$V = 100$ mL

$$\underset{\substack{100\text{ mL}\\2\text{ M}}}{H_3PO_2} + \underset{\substack{1\text{ M}\\V=?}}{NaOH} \rightarrow NaH_2PO_2 + H_2O$$

Millimoles of $H_3PO_2 = M \times V = 2 \times 100 = 200$

For 1 millimole of H_3PO_2, we require 1 millimoles of NaOH.

For 200 millimole of H_3PO_2, we require 200 millimoles of NaOH.

So, volume of NaOH = 200 mL

06 A 6.50 molal solution of KOH (*aq*) has a denisity of 1.89 g cm^{-3}. The molarity of the solution is ..... mol dm^{-3} (Round off to the nearest integer).

[Atomic masses: K : 39.0 u, O : 16.0u, H : 1.0 u]

[2021, 16 March Shift-I]

Ans. ***(9)***

$$\text{Molality}(m) = \frac{M \times 1000}{\{(1000d) - M \times M_{\text{solute}}\}}$$

where, M = molarity

d = density of solution

M_{solute} = molar mass of solute

Putting the values,

$$6.50 = \frac{M \times 1000}{(1000 \times 1.89) - (M \times 56)}$$

On solving, $M = \frac{12285}{1364}$

$M = 9$ molar

07 4.5 g of compound *A* (MW = 90) was used to make 250 mL of its aqueous solution. The molarity of the solution in *M* is $x \times 10^{-1}$. The value of *x* is ..... . (Rounded off to the nearest integer).

[2021, 24 Feb Shift-I]

Ans. ***(2)***

Given, weight of compound *A* = 4.5 g

Molecular weight of compound *A* = 90 g/mol

Volume of solution (in mL) = 250 mL

Now, molarity is defined as number of moles of solute or compound *A* divided by volume of solution (in L).

$$M = \frac{\text{Number of moles of solute}(n)}{\text{Volume of solution}}$$

$$= \frac{\frac{4.5}{90}}{\frac{250}{1000}} = 0.2 \text{ or } = 2 \times 10^{-1}\text{ M}$$

$$\therefore \quad n = \frac{\text{Weight of solute (compound } A)}{\text{Molecular weight of solute (compound } A)}$$

Hence, $x \times 10^{-1}$ μ

$x = 2$

08 A solution of two components containing n_1 moles of the 1st component and n_2 moles of the 2nd component is prepared. M_1 and M_2 are the molecular weights of component 1 and 2 respectively. If *d* is the density of the solution in g mL^{-1}, C_2 is the molarity and χ_2 is the mole-fraction of the 2nd component, then C_2 can be expressed as **[2020, 6 Sep Shift-I]**

(a) $C_2 = \frac{1000\,\chi_2}{M_1 + \chi_2 (M_2 - M_1)}$

(b) $C_2 = \frac{d\chi_2}{M_2 + \chi_2 (M_2 - M_1)}$

(c) $C_2 = \frac{1000\,d\chi_2}{M_1 + \chi_2 (M_2 - M_1)}$]

(d) $C_2 = \frac{d\chi_1}{M_2 + \chi_2 (M_2 - M_1)}$

Ans. ***(c)***

In first component,

Mass = number of moles × molecular weight = n_1M_1

In second component,

Mass = n_2M_2

Mass of solution = $n_1M_1 + n_2M_2$ ...(i)

Mole-fraction $(\chi_2) = \frac{n_2}{n_1 + n_2}$

$$\therefore \quad n_1 = \frac{n_2(1 - \chi_2)}{\chi_2} \quad \text{...(ii)}$$

Place the value of n_1 in eq. (i)

$$\therefore \quad \frac{n_2(1 - \chi_2)M_1}{\chi_2} + n_2M_2$$

$$\Rightarrow \quad \frac{n_2}{\chi_2}(M_2\chi_2 - M_1\chi_2 + M_1)$$

Volume of solution,

$$= \frac{n_2(M_2\chi_2 - M_1\chi_2 + M_1)}{1000 \times d \times \chi_2}\text{ L}$$

$$C_2 = \frac{1000 \times n_2 \times d\chi_2}{n_2(M_2\chi_2 - M_1\chi_2 + M_1)}$$

$$\therefore \quad C_2 = \frac{1000d\,\chi_2}{M_1 + \chi_2(M_2 - M_1)}$$

Hence, the correct option is (c).

09 The hardness of a water sample containing 10^{-3} M $MgSO_4$ expressed as $CaCO_3$ equivalents (in ppm) is.....

(molar mass of $MgSO_4$ is 120.37 g/mol) **[2020, 9 Jan Shift-II]**

Ans. ***(100)***

Hardness in ppm

$$= \frac{\text{Mass of } CaCO_3 \text{ equivalent to the total number of moles of hardness causing substances} \times 10^6}{\text{Mass of water sample}}$$

Here, $[Mg^{2+}] = 10^{-3}$ M

$n_{Mg^{2+}} = 10^{-3}$ per 1 L water $\cong 1000$ g

Mass of 10^{-3} moles of $CaCO_3 = 10^{-3} \times 100$ g $= 0.1$ g

$$\therefore \quad \text{ppm} = \frac{0.1 \times 10^6}{1000} = 100 \text{ ppm}$$

10 10.30 mg of O_2 is dissolved into a litre of sea water of density 1.03 g/mL. The concentration of O_2 in ppm is **[2020, 9 Jan Shift-II]**

Ans. ***(10.00)***

Mass of $O_2 = 10.30$ mg (Given)

Mass of sea water solution

= volume × density

$= 1\text{ L} \times 1.03\text{ g/mL}$

$= 1000\text{ mL} \times 1.03\text{ g mL}^{-1} = 1030$ g

$$\text{ppm} = \frac{\text{mass of } O_2}{\text{mass of solution}} \times 10^6$$

$$= \frac{10.30 \times 10^{-3}\text{ g} \times 10^6}{1030\text{ g}}$$

$= 10$ ppm

11 What would be the molality of 20% (mass/mass) aqueous solution of KI?

Molar mass of KI = 166 g mol^{-1})

[2019, 9 April Shift-II]

(a) 1.48 (b) 1.51 (c) 1.35 (d) 1.08

Ans. ***(b)***

Key Idea Molality is defined as number of moles of solute per kg of solvent.

$$m = \frac{w_2}{Mw_2} \times \frac{1000}{w_1}$$

w_2 = mass of solute

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Mw_2 = molecular mass of solute
w_1 = mass of solvent.

The molality of 20% (mass/mass) aqueous solution of KI can be calculated by following formula.

$$m = \frac{w_2 \times 1000}{Mw_2 \times w_1}$$

20% aqueous solution of KI means that 20 gm of KI is present in 80 gm solvent.

$$m = \frac{20}{166} \times \frac{1000}{80} = 1.506 \approx 1.51 \text{ mol/kg}$$

12 The mole fraction of a solvent in aqueous solution of a solute is 0.8. The molality (in mol kg^{-1}) of the aqueous solution is **[2019, 12 April Shift-I]**

(a) 13.88×10^{-2} (b) 13.88×10^{-1}
(c) 13.88 (d) 13.88×10^{-3}

Ans. ***(c)***

Key Idea

$$\text{Molality}(m) = \frac{\text{Mass of solute}(w_2) \times 1000}{\text{Molar mass of solute}(M_2) \times \text{mass of solvent}(w_1)}$$

$$m = \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

and also, $m = n_2 \times \frac{1000}{n_1 \times M_1}$

$X_{\text{solvent}} = 0.8$ (Given)

It means that $n_{\text{solvent}}(n_1) = 0.8$

and $n_{\text{solute}}(n_2) = 0.2$

Using formula $m = n_2 \times \frac{1000}{n_1 \times M_1}$

$$= 0.2 \times \frac{1000}{0.8 \times 18} = 13.88 \text{ mol kg}^{-1}$$

13 A solution of sodium sulphate contains 92 g of Na^+ ions per kilogram of water. The molality of Na^+ ions in that solution in mol kg^{-1} is **[2019, 9 Jan Shift-I]**

(a) 16 (b) 4
(c) 132 (d) 8

Ans. ***(b)***

$$\text{Molality}(m) = \frac{\text{Number of moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

$$= \frac{\text{Mass of solute (in g)} \times 1000}{\left[\begin{array}{c}\text{Molecular weight of solute} \\ \times \text{ mass of solvent (in g)}\end{array}\right]}$$

$$= \frac{w_{Na^+} \times 1000}{M_{Na^+} \times w_{H_2O}} = \frac{92 \times 1000}{23 \times 1000} = 4 \text{ mol kg}^{-1}$$

14 The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is

(a) 17.1 g (b) 68.4 g
(c) 136.8 g (d) 34.2 g **[2019, 10 Jan Shift-II]**

Ans. ***(b)***

$$\text{Molarity} = \frac{\text{Number of moles of solute}(n)}{\text{Volume of solution (in L)}}$$

Also, $n = \frac{w_B(\text{g})}{M_B(\text{g mol}^{-1})}$

$\therefore$ $\text{Molarity} = \frac{w_B / M_B}{V}$

Given, w_B = mass of solute (B) in g

M_B = Gram molar mass of B ($C_{12}H_{22}O_{11}$)

$= 342 \text{ g mol}^{-1}$

Molarity = 0.1 M, Volume (V) = 2 L

$\Rightarrow$ $0.1 = \frac{w_B / 342}{2}$

$\Rightarrow$ $w_B = 0.1 \times 342 \times 2 \text{ g} = 68.4 \text{ g}$

15 8 g of NaOH is dissolved in 18 g of H_2O. Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solution respectively are

(a) 0.2, 11.11 (b) 0.167, 22.20
(c) 0.2, 22.20 (d) 0.167, 11.11 **[2019, 12 Jan Shift-II]**

Ans. ***(d)***

Mole fraction of solute

$$= \frac{\text{number of moles of solute} + \text{number of moles solvent}}{\text{number of moles of solute}}$$

$$\chi_{\text{Solute}} = \frac{n_{\text{Solute}}}{n_{\text{Solute}} + n_{\text{Solvent}}}$$

$$= \frac{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}}}{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}} + \frac{w_{\text{Solvent}}}{Mw_{\text{Solvent}}}}$$

Given, $w_{\text{Solute}} = w_{\text{NaOH}} = 8 \text{ g}$

$Mw_{\text{Solute}} = Mw_{\text{NaOH}} = 40 \text{ g mol}^{-1}$

$w_{\text{Solvent}} = w_{H_2O} = 18 \text{ g}$

$Mw_{\text{Solvent}} = 18 \text{ g mol}^{-1}$

$$\therefore \chi_{\text{Solute}} = \chi_{\text{NaOH}} = \frac{\frac{8}{40}}{\frac{8}{40} + \frac{18}{18}}$$

$$= \frac{0.2}{0.2 + 1} = \frac{0.2}{1.2} = 0.167$$

Now, molality

$$(m) = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

$$= \frac{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}}}{w_{\text{Solvent}}(\text{in g})} \times 1000$$

$$= \frac{\frac{8}{40}}{18} \times 1000 = \frac{0.2}{18} \times 1000 = 11.11 \text{ mol kg}^{-1}$$

Thus, mole fraction of NaOH in solution and molality of the solution respectively are 0.167 and 11.11 mol kg^{-1}

16 A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution ? **[AIEEE 2011]**

(a) 0.100 (b) 0.190
(c) 0.086 (d) 0.050

Ans. ***(c)***

5.2 molal aqueous solution of CH_3OH suggests that 5.2 moles of CH_3OH are dissolved in 1000 g of water.

$n_1(CH_3OH) = 5.2$

$n_2(H_2O) = \frac{1000}{18} = 55.56$

$\therefore$ $n_1 + n_2 = 5.20 + 55.56$

$= 60.76$ mol

$\therefore$ X_{CH_3OH} = Mole fraction of CH_3OH

$$= \frac{n_1}{n_1 + n_2} = \frac{5.2}{60.76} = 0.086$$

17 The molality of a urea solution in which 0.0100 g of urea, [$(NH_2)_2CO$] is added to 0.3000 dm^3 of water at STP is **[AIEEE 2011]**

(a) 0.555 m (b) 5.55×10^{-4} m
(c) 33.3 m (d) 3.33×10^{-2} m

Ans. ***(b)***

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kg of water}}$$

Moles of urea = $\frac{0.010}{60}$ mol

Water at STP ($d = 1 \text{ g/cm}^3 = 1 \text{ kg/dm}^3$)

$= 0.3 \text{ dm}^3 = 0.3$ kg

$\therefore$ $\text{Molality} = \frac{0.010}{60 \times 0.3} = 5.55 \times 10^{-4}$ m

18 The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be **[AIEEE 2007]**

(a) 1.64 (b) 1.88 (c) 1.22 (d) 1.45

Ans. ***(c)***

$$\text{Molarity} = \frac{10 \times \text{density} \times \% \text{ by wt. of solute}}{\text{mol wt. of the solute}}$$

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$$\text{Density} = \frac{3.60 \times 98}{10 \times 29}$$
$$= 1.216\ \text{gML}^{-1} = 1.22\ \text{gML}^{-1}$$

19 Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is **[AIEEE 2007]**

(a) $\frac{2}{3}$ (b) $\frac{1}{3} \times \frac{273}{298}$

(c) $\frac{1}{3}$ (d) $\frac{1}{2}$

Ans. ***(c)***

Suppose the equal mass of methane and oxygen = w = 1g

$$\text{Mole fraction of oxygen} = \frac{w/32}{w/32 + w/16}$$
$$= \frac{1/32}{3/32} = \frac{1}{3}$$

Let the total pressure = p

Pressure exerted by oxygen (partial pressure)

$$= X_{O_2} \times p_{\text{total}} = p \times \frac{1}{3}$$

Thus, the fraction of the total pressure exerted by oxygen is 1/3.

20 Density of a 2.05 M solution of acetic acid in water is 1.02 g / mL. The molality of the solution is **[AIEEE 2006]**

(a) 1.14 mol kg^{-1} (b) 3.28 mol kg^{-1}

(c) 2.28 mol kg^{-1} (d) 0.44 mol kg^{-1}

Ans. ***(c)***

$$\text{Molality}\,(m) = \frac{M}{1000\,d - MM_1} \times 100$$

M = Molarity; M_1 = Molecular mass

d = density

$$= \frac{2.05}{(1000 \times 1.02) - (2.05 \times 60)} \times 1000$$
$$= 2.28\ \text{mol kg}^{-1}$$

21 Two solutions of a substance (non-electrolyte) are mixed in the following manner. 480 mL of 1.5 M first solution + 520 mL of 1.2 M second solution.

What is the molarity of the final mixture ? **[AIEEE 2005]**

(a) 2.70 M (b) 1.34 M

(c) 1.50 M (d) 1.20 M

Ans. ***(b)***

The molarity of the resulting solution is given by

$$\text{Total molarity} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$
$$= \frac{1.5 \times 480 + 1.2 \times 520}{480 + 520} = 1.34\ \text{M}$$

22 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of urea solution is (Avogadro constant, $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$) **[AIEEE 2004]**

(a) 0.001 M (b) 0.01 M

(c) 0.02 M (d) 0.1 M

Ans. ***(b)***

Avogadro's number, N_A

$= 6.02 \times 10^{23}$ molecules = 1 mol

$\therefore 6.02 \times 10^{20}$ molecules = 0.001 mol in 100 mL or (0.1 L) solution

$$\therefore \text{Molar concentration} = \frac{\text{mol}}{\text{volume in litre}}$$
$$= \frac{0.001}{0.1} = 0.01\ \text{M}$$

23 To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the volume of 0.1 M aqueous KOH solution required is **[AIEEE 2004]**

(a) 10 mL (b) 20 mL

(c) 40 mL (d) 60 mL

Ans. ***(c)***

H_3PO_3 is a dibasic acid (*i.e.*, contains two ionisable protons attached directly to O).

$$H_3PO_3 \rightleftharpoons 2H^+ + HPO_4^{2-}$$

$\therefore$ 0.1 M H_3PO_3 = 0.2 N H_3PO_3

and 0.1 M KOH = 0.1 N KOH

$$\underset{(KOH)}{N_1V_1} = \underset{(H_3PO_3)}{N_2V_2}$$

$$0.1\,V_1 = 0.2 \times 20;\ V_1 = 40\ \text{mL}$$

24 25 mL of a solution of barium hydroxide on titration with 0.1 molar solution of hydrochloric acid gave a titre value of 35 mL. The molarity of barium hydroxide solution was **[AIEEE 2003]**

(a) 0.07 (b) 0.14

(c) 0.28 (d) 0.35

Ans. ***(a)***

Let molarity of $Ba(OH)_2 = M_1$

$\therefore$ Normality $= 2M_1$

Molarity of HCl = 0.1 M = 0.1 N_2

$$N_1V_1 = N_2V_2$$
$$2M_1 \times 25 = 0.1 \times 35$$
$$M_1 = 0.07\ \text{M}$$

25 Which of the following concentration factor is affected by change in temperature? **[AIEEE 2002]**

(a) Molarity (b) Molality

(c) Mole fraction (d) Weight fraction

Ans. ***(a)***

Molarity gets affected as it is the number of moles per unit volume (volume increases with increase in temperature).

TOPIC 2
Henry's Law and Raoult's Law

26 CO_2 gas is bubbled through water during a soft drink manufacturing process at 298 K. If CO_2 exerts a partial pressure of 0.835 bar then x m mol of CO_2 would dissolve in 0.9 L of water. The value of x is ..... . (Nearest integer)

(Henry's law constant for CO_2 at 298 K is 1.67×10^3 bar)

[2021, 25 July Shift-I]

Ans. ***(25)***

According to Henry's law,

$$p_{CO_2} = K_H\,X_{CO_2}$$

p_{CO_2}, K_H and X_{CO_2} are pressure of CO gas. Henry's constant and mole fraction of CO respectively.

$$\Rightarrow \quad X_{CO_2} = \frac{p_{CO_2}}{K_H} \qquad \ldots(i)$$

Given, $K_H = 0.835 \times 2 \times 10^3$ bar

$$= 1.67 \times 10^3\ \text{bar}$$
$$p_{CO_2} = 0.835\ \text{bar}$$

Put all values in equation (i), we get

$$X_{CO_2} = \frac{0.835}{0.835 \times 10^3 \times 2}$$
$$X_{CO_2} = 0.5 \times 10^{-3}$$

Volume of water = 0.9 L = 900 mL

Density of water = 1 g/mL

Mass of water = density × volume = 900 g

So, number of mole of water

$$= \frac{900}{18} = 50\ \text{moles}$$

So, $\frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = 0.5 \times 10^{-3}$

$n_{CO_2} << H_2O = 50$ moles

So, ${}^{n}CO_2 + n_{H_2O} = {}^{n}H_2O$

$$n_{CO_2} = 0.5 \times 10^{-3} \times 50$$
$$= 25 \times 10^{-3}\ \text{mol}$$

Millimoles of $CO_2 = 0.025 \times 1000 = 25$

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27 The vapour pressures of *A* and *B* at 25°C are 90 mm Hg and 15 mm Hg respectively. If *A* and *B* are mixed such that the mole-fraction of *A* in the mixture is 0.6, then the mole fraction of *B* in the vapour phase is $x \times 10^{-1}$. The value of *x* is ..... . (Nearest integer)

[2021, 20 July Shift-II]

Ans. ***(1)***

Partial pressure of *A*, $p_A^\circ = 90$ mm of Hg

Partial pressure of *B*, $p_B^\circ = 15$ mm of Hg

Mole fraction of *A*, $\chi_A = 0.6$

Mole fraction of *B*, $\chi_B = 0.4$

Total pressure,

$$p_T = \chi_A p_A^\circ + \chi_B p_B^\circ$$
$$= (0.6 \times 90) + (0.4 \times 15)$$
$$= 54 + 6 = 60 \text{ mm}$$

Now, mole fraction of *B* in vapour phase,

i.e. $Y_B = \frac{p_B}{p_T} = \frac{\chi_B p_B^\circ}{60} = 0.1 = 1 \times 10^{-1}$

$x = 1$

28 At 20°C, the vapour pressure of benzene is 70 torr and that of methyl benzene is 20 torr. The mole fraction of benzene in the vapour phase at 20°C above an equimolar mixture of benzene and methyl benzene is..... $\times 10^{-2}$. (Nearest integer)

[2021, 20 July Shift-I]

Ans. ***(78)***

Vapour pressure of pure benzene, $p_A^\circ = 70$ Torr

Vapour pressure of pure methyl benzene, $p_B^\circ = 20$ Torr

This mixture is equimolar, so, number of moles of benzene, n_A = number of moles of methyl benzene, n_B

Mole fraction of benzene in vapour phase,

$$y_A = \frac{p_A}{p_T} \quad ...(i)$$

where p_A is pressure of benzene in mixture.

$$p_A = \underset{\text{Mole fraction}}{p_A^\circ \chi_A}$$
$$= p_A^\circ \times \frac{n_A}{n_A + n_B} = p_A^\circ \times \frac{\frac{n}{A}}{2\frac{n}{A}} = \frac{p_A^\circ}{2}$$

p_T is total pressure,

$$p_T = p_A^\circ \chi_A + \underset{\text{(pressure of methyl benzene)}}{p_B^\circ \chi_B} = p_A + p_B$$

$$p_T = \frac{p_A^\circ}{2} + \frac{p_B^\circ}{2} = \frac{p_A^\circ + p_B^\circ}{2}$$

Putting in above equation (i),

$$y_A = \frac{\frac{70}{2}}{\frac{(70+20)}{2}} = \frac{70}{90}$$

$$y_A = 0.78 = 78 \times 10^{-2}$$

29 At 300 K, the vapour pressure of a solution containing 1 mole of *n*-hexane and 3 moles of *n*-heptane is 550 mm of Hg. At the same temperature, if one more mole of *n*-heptane is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. What is the vapour pressure in mm Hg of *n*-heptane in its pure state ..... ?

[2020, 4 Sep Shift-I]

Ans. ***(600)***

Given,

Vapour pressure of solution = 550 mmHg

Mole of hexane (n_{hex}) = 1 mol

Mole of heptane (n_{hep}) = 3 mol

From Raoult's law,

Vapour pressure in solution = vapour pressure of pure solvent × mole fraction

$$p = p^\circ \chi$$

Here, vapour pressure of solution = *p*, vapour pressure of pure solvent = p° and mole fraction = χ

Total vapour pressure of solution,

$$p_{total} = p^\circ_{hex}\, \chi_{hex} + p^\circ_{hep}\, \chi_{hep}$$

Case I Mole fraction of hexane,

$$\chi_{hex} = \frac{1}{1+3} = 0.25$$

Mole fraction of heptane,

$$\chi_{hep} = \frac{3}{1+3} = 0.75$$

$$p = p^\circ_{hex} 0.25 + p^\circ_{hep} \times 0.75$$
$$550 = p^\circ_{hex} 0.25 + p^\circ_{hep} \times 0.75 \quad ...(i)$$

Case II According to question, when 1 mole of heptane added and vapour pressure increased by 10 mm of Hg.

Mole fraction of hexane,

$$\chi_{hex} = \frac{1}{1+4} = 0.20$$

Mole fraction of heptane,

$$\chi_{hep} = \frac{4}{1+4} = 0.80$$

$$p = p^\circ_{hex}\, \chi_{hex} + p^\circ_{hep}\, \chi_{hep}$$

Vapour pressure increased by 10 mm of Hg then $p = 560$

$$\Rightarrow 560 = p^\circ_{hex} 0.20 + p^\circ_{hep} 0.80 \quad ...(ii)$$

Eq. (i) multiplied by 0.20

$$\Rightarrow 550 \times 0.20 = (0.25 \times 0.20) p^\circ_{hex} + (0.75 \times 0.20) p^\circ_{hep}$$
$$\Rightarrow 110 = 0.05 p^\circ_{hex} + 0.15 p^\circ_{hep} \quad ...(iii)$$

Eq. (ii) multiplied by 0.25,

$$\Rightarrow 560 \times 0.25 = (0.20 \times 0.25) p^\circ_{hex} + (0.8 \times 0.25) p^\circ_{hep}$$
$$140 = 0.05 p^\circ_{hex} + 0.20 p^\circ_{hep} \quad ...(iv)$$

Now, Eq. (iii) and Eq. (iv)

$$\Rightarrow 0.05 p^\circ_{hex} + 0.15 p^\circ_{hep} - 0.05 p^\circ_{hex} - 0.20 p^\circ_{hep} = 110 - 140$$
$$\Rightarrow 0.15 p^\circ_{hep} - 0.20 p^\circ_{hep} = -30$$
$$\Rightarrow -0.05 p^\circ_{hep} = -30$$
$$\Rightarrow p^\circ_{hep} = \frac{30}{0.05} = 600 \text{ mm of Hg}$$

Thus, vapour pressure of pure *n*-heptane (p°_{hep}) is 600 mm of Hg.

30 Henry's constant (in kbar) for four gases α, β, γ and δ in water at 298 K is given below :

	α	β	γ	δ
K_H	50	2	2×10^{-5}	0.5

(density of water = 10^3 kg m^{-3} at 298 K). This table implies that

[2020, 3 Sep Shift-I]

(a) α has the highest solubility in water at a given pressure

(b) solubility of γ at 308 K is lower than at 298 K

(c) The pressure of a 55.5 molal solution of γ is 1 bar

(d) The pressure of a 55.5 molal solution of δ is 250 bar

Ans. ***(d)***

Henry's equation for solubility (*S*) of a gas (β) in a liquid is expressed in terms of mole- fraction of the gas (χ_B) at a given temperature,

$$p = K_H \times \chi_B = K_H \times S$$

So, solubility of gas, $S \propto \frac{1}{K_H}$ at *T*(K) and given pressure.

Order of solubility of the gases (high the value of K_H, lower is the solubility) :

$$\gamma > \delta > \beta > \alpha$$

So, option (a) is not correct.

Again, $K_H \propto$ temperature, i.e. solubility of the gas will decrease with increase in temperature also.

But this conclusion cannot be drawn from table.

So, option (b) is not correct.

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We know, mole-fraction of a solute (B) in a binary aqueous solution,

$$\chi_B = \frac{18\,m}{1000 + 18\,m}$$

[$\because m$ = molality]

For γ at $m = 55.5$ molal

$$p = K_H^{\gamma} \times m = (2 \times 10^{-5}) \times \left(\frac{18 \times 55.5}{1000 + 18 \times 55.5}\right)$$

$= 1.81 \times 10^{-5}$ K bar $= 1.8 \times 10^{-2}$ bar

So, option (c) is not correct.

For δ at $m = 55.5$ molal

$$p = K_H^{\delta} = (0.5) \times \left(\frac{18 \times 55.5}{1000 + 18 \times 55.5}\right)$$

$= 0.2498$ k bar $\simeq 250$ bar

So, option (d) is correct.

31 At 35°C, the vapour pressure of CS_2 is 512 mm Hg and that of acetone is 344 mm Hg. A solution of CS_2 in acetone has a total vapour pressure of 600 mm Hg. The false statement amongst the following is **[2020, 7 Jan Shift-I]**

(a) Raoult's law is not obeyed by this system
(b) CS_2 and acetone are less attracted to each other than to themselves
(c) a mixture of 100 mL CS_2 and 100 mL acetone has a volume < 200 mL
(d) heat must be absorbed in order to produce the solution at 35°C

Ans. ***(c)***

The incorrect statement among the given statements is (c) and the explanation of all the statements is as follows :

According to Raoult's law, vapour pressure of the solution p_{id} (ideal vapour pressure) $= p_A° + (p_B° - p_A°)x_B$

(A = solvent : acetone, B = solute : CS_2)

Given; $p_A° = 344$ mm Hg.

$p_B° = 512$ mm Hg.

$\therefore \quad p_{id} = 344 + (512 - 344)x_B$

or $\quad p_{id} = 344 + 168\,x_B$

and so, $0 < x_B < 1$.

Also, total vapour pressure (p) $= 600$ mmHg

$\therefore$ For any value of x_B, $p > p_{id}$.

Since $p \neq p_{id}$, so, option (a) is correct.

Option (b) is also correct. Since $p > p_{id}$, (i.e. positive deviation) therefore attractive force between CS_2 and acetone is weaker than $CS_2 - CS_2$ or acetone-acetone attraction.

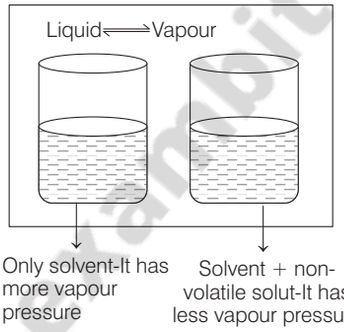
Option (c) is incorrect as for positive deviation, $\Delta V > 0$ because final volume of solution must be greater than the sum of volumes of components taken.

Option (d) is correct. Since, in such solution, $\Delta_{mix}H$ is positive because energy is required to break A—A and B—B bonds.

32 Two open beakers one containing a solvent and the other containing a mixture of that solvent with a non-volatile solute are together sealed in a container. Over time **[2020, 7 Jan Shift-II]**

(a) the volume of the solution decreases and the volume of the solvent increases
(b) the volume of the solution does not change and the volume of the solvent decreases
(c) the volume of the solution increases and the volume of the solvent decreases
(d) the volume of the solution and the solvent does not change

Ans. ***(c)***



If a non-volatile solute is added to a solvent to form a solution, the vapour pressure gets decreased.

$\therefore$ According to Raoult's law, if vapour pressure of pure solvent is $p°$, vapour pressure of solvent in solution (p) is $= p° \cdot x_A$.

$\therefore \qquad p < p°$

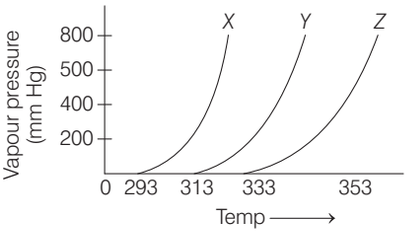
Since, vapour pressure of solution is less, there will be net backward reaction [i.e. vapour ⟶ liquid] in that beaker.

Thus, its volume increases.

In another beaker containing only net reaction is forward,

Thus, volume decreases.

33 A graph of vapour pressure and temperature for three different liquids X, Y, and Z is shown below : **[2020, 8 Jan Shift-I]**



The following inference are made :

A. X has higher intermolecular interactions compared to Y.
B. X has lower intermolecular interactions compared to Y.
C. Z has lower intermolecular interactions compared to Y.

The correct inference(s) is/are :

(a) (C) (b) (B)
(c) (A) (d) (A) and (C)

Ans. ***(b)***

From given graph it can be seen that , X has higher vapour pressure as compared to Y at lower temperature (or to attain same vapour pressure, Y need higher temperature than X). It means that intermolecular interactions must be weaker in X as compared to Y, which further must be weaker than Z by the same reason also. Hence, option (b) is correct.

34 The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298 K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is 0.5 in the mixture. The vapour pressure of the final solution, the mole fractions of components A and B in vapour phase, respectively are **[2019, 8 April Shift-I]**

(a) 450 mmHg, 0.4, 0.6
(b) 500 mmHg, 0.5, 0.5
(c) 450 mmHg, 0.5,0.5
(d) 500 mmHg, 0.4,0.6

Ans. ***(d)***

According to Dalton's law of partial pressure $p_{total} = p_A + p_B$

$$= p_A^{\circ}\chi_A + p_B^{\circ}\chi_B \qquad \ldots(i)$$

Given, $p_A^{\circ} = 400$ mm Hg, $p_B^{\circ} = 600$ mm Hg

$\chi_B = 0.5$, $\chi_A + \chi_B = 1$

$\therefore \quad \chi_A = 0.5$

On substituting the given values in Eq. (i). We get,

$p_{total} = 400 \times 0.5 + 600 \times 0.5 = 500$ mm Hg

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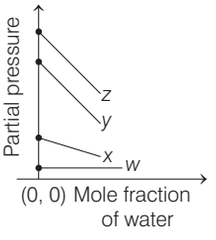
Mole fraction of A in vapour phase,

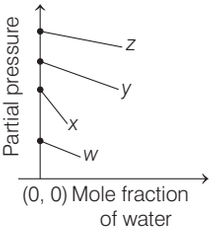
$$Y_A = \frac{p_A}{p_{total}} = \frac{p_A^\circ \chi_A}{p_{total}} = \frac{0.5 \times 400}{500} = 0.4$$

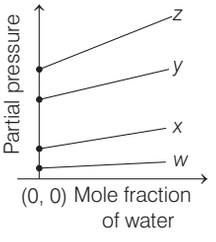
Mole of B in vapour phase,

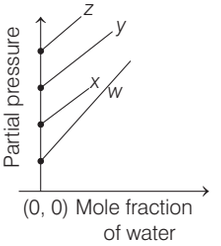
$$Y_A + Y_B = 1$$
$$Y_B = 1 - 0.4 = 0.6$$

35 For the solution of the gases w, x, y and z in water at 298 K, the Henry's law constants (K_H) are 0.5, 2, 35 and 40 K bar, respectively. The correct plot for the given data is **[2019, 8 April Shift-II]**

(a)


(b)


(c)


(d)


Ans. ***(a)***

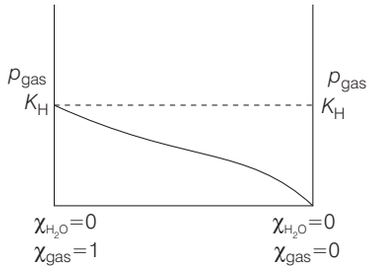
According to Henry's law (at constant temperature)

$$p_{gas} = K_H \times \chi_{gas(solute)}$$
$$= K_H \times [1 - \chi_{H_2O(solvent)}]$$
$$p_{gas} = K_H - K_H \chi_{H_2O}$$

p_{gas} = partial pressure of the gas above its solution with a liquid (solvent) say water.

χ_{gas} = mole fraction of the gas (solute) in the solution.

χ_{H_2O} = mole fraction of water (solvent).



[i.e. $p_{gas} = K_H$] Higher the value of K_H, higher will be the partial pressure of the gas (p_{gas}), at a given temperature. The plot of p_{gas} *vs* χ_{H_2O} gives a (–ve) slope.

$$p_{gas} = K_H - K_H \times \chi_{H_2O}$$

Comparing the above equation with the equation of straight line $y = mx + c$

Slope $= -K_H$, intercept $= K_H$

So, (i) Higher the value of K_H, more (–ve) will be the slope and it is for z ($K_H = 40$ K bar)

(ii) Higher the value of K_H, higher with the value of intercept, i.e. partial pressure and it is also for z.

36 Liquid M and liquid N form an ideal solution. The vapour pressures of pure liquids M and N are 450 and 700 mmHg, respectively, at the same temperature. Then correct statement is **[2019, 9 April Shift-I]**

x_M = mole fraction of M in solution;

x_N = mole fraction of N in solution;

y_M = mole fraction of M in vapour phase;

y_N = mole fraction of N in vapour phase

(a) $\frac{x_M}{x_N} > \frac{y_M}{y_N}$

(b) $\frac{x_M}{x_N} = \frac{y_M}{y_N}$

(c) $\frac{x_M}{x_N} < \frac{y_M}{y_N}$

(d) $(x_M - y_M) < (x_N - y_N)$

Ans. ***(a)***

Key Idea For a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. This is known as Raoult's law.

Liquid M and N form an ideal solution. Vapour pressures of pure liquids M and N are 450 and 700 mm Hg respectively.

$\therefore \quad p^\circ_N > p^\circ_M$

So, by using Raoult's law

$$y_N > x_N \quad ...(i)$$

and $$x_M > y_M \quad ...(ii)$$

Multiplying (i) and (ii) we get

$$y_N\, x_M > y_M\, x_N$$

$$\therefore \quad \frac{x_M}{x_N} > \frac{y_M}{y_N}$$

Thus, correct relation is (a).

37 Which one of the following statements regarding Henry's law is not correct?

(a) Different gases have different K_H (Henry's law constant) values at the same temperature

(b) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids

(c) The value of K_H increases with increase of temperature and K_H is function of the nature of the gas

(d) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution **[2019, 9 Jan Shift-I]**

Ans. ***(b)***

At constant temperature, solubility of a gas (S) varies inversely with Henry's law constant (K_H)

$$K_H = \frac{\text{Pressure}}{\text{Solubility of a gas in a liquid}} = \frac{P}{S}$$

Thus, higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

38 Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapour pressures of pure A and pure B are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapour in equilibrium with a solution containing 40 mole percent of A at this temperature is

(a) $x_A = 0.76$; $x_B = 0.24$

(b) $x_A = 0.28$; $x_B = 0.72$

(c) $x_A = 0.4$; $x_B = 0.6$

(d) $x_A = 0.37$; $x_B = 0.63$ **[2019, 10 Jan Shift-I]**

Ans. ***(b)***

For ideal solution,

$$p = x'_A\, p^\circ_A + x'_B\, p^\circ_B$$

$\because \quad x'_A = 0.4$, $x'_B = 0.6$

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$p°_A = 7 \times 10^3$ Pa, $p°_B = 12 \times 10^3$ Pa

On substituting the given values in Eq. (i), we get

$$p = 0.4 \times 7 \times 10^3 + 0.6 \times 12 \times 10^3$$
$$= 10 \times 10^3 \text{ Pa} = 1 \times 10^4 \text{ Pa}$$

In vapour phase,

$$x_A = \frac{p_A}{p} = \frac{x'_A p°_A}{p} = \frac{0.4 \times 7 \times 10^3}{1 \times 10^4} = 0.28$$

$\therefore \quad x_B = 1 - 0.28 = 0.72 \quad [\because x_A + x_B = 1]$

39 On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa, respectively. Vapour pressure of the solution obtained by mixing 25 g of heptane and 35 g of octane will be (molar mass of heptane $= 100$ g mol^{-1} and of octane $= 114$ g mol^{-1}). **[AIEEE 2010]**

(a) 72.0 kPa (b) 36.1 kPa
(c) 96.2 kPa (d) 144.5 kPa

Ans. ***(a)***

$$p_T = X_H \cdot p°_H + X_0 \cdot p°_0$$
$$X_H = \frac{25/100}{25/100 + 35/114} = 0.45$$

$\therefore \quad X_0 = 0.55$

$$p_T = 0.45 \times 105 + 0.55 \times 45$$
$$= 72.0 \text{ kPa}$$

40 Two liquids *X* and *Y* form an ideal solution at 300 K, vapour pressure of the solution containing 1 mol of *X* and 3 mol of *Y* is 550 mmHg. At the same temperature, if 1 mol of *Y* is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mmHg) of *X* and *Y* in their pure states will be, respectively **[AIEEE 2009]**

(a) 200 and 300 (b) 300 and 400
(c) 400 and 600 (d) 500 and 600

Ans. ***(c)***

$$p_T = p_A° X_A + p_B° X_B$$
$$550 = p_A° \times \frac{1}{4} + p_B° \times \frac{3}{4}$$

Thus, $p_A° + 3p_B° = 2200$ ...(i)

When 1 mole of *Y* is further added to the solution, vapour pressure of a solution becomes 560 mm Hg.

Thus, $560 = p_A° \times \frac{1}{5} + p_B° \times \frac{4}{5}$

Thus, $p_A° + 4p_B° = 2800$ ...(ii)

On subtracting Eq. (ii) by Eq. (i), we get

$$p_B° = 2800 - 2200$$
$$\Rightarrow \quad p_B° = 600$$

Putting the value of $p_B°$ in Eq. (i)

$$p_A° + 3 \times 600 = 2200$$
$$p_A° = 2200 - 1800 = 400$$

41 A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? **[AIEEE 2009]**

(a) The solution formed is an ideal solution
(b) The solution is non-ideal, showing positive deviation from Raoult's law
(c) The solution is non-ideal, showing negative deviation from Raoult's law
(d) *n*-heptane shows positive deviation while ethanol show negative deviation from Raoult's law

Ans. ***(b)***

n-heptane and ethanol forms non-ideal solution. As a result, *n*-heptane-ethanol molecular interaction is very poor in comparison to ethanol-ethanol or *n*-heptane so the resulting gives positive deviation from Raoult's law.

42 A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be **[AIEEE 2007]**

(a) 350 (b) 300
(c) 700 (d) 360

Ans. ***(a)***

According to Raoult's law,

$$p = p°_A X_A + p°_B X_B$$
$$290 = 200 \times 0.4 + p°_B \times 0.6$$
$$p°_B = 350 \text{ mm}$$

43 Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is **[AIEEE 2005]**

(a) 53.5 (b) 37.5
(c) 25 (d) 50

Ans. ***(d)***

Mixture contains 78 g benzene = 1 mol benzene and 46 g toluene = 0.5 mol toluene

Total moles of benzene and toluene $= 1.5$ mol

Mole fraction of benzene in mixture

$$= \frac{1}{1.5} = \frac{2}{3}$$

Vapour pressure of benzene

$$p_b° = 75 \text{ torr}$$

$\therefore$ Partial vapour pressure of benzene

$$= p°_b X_b$$
$$= 75 \times \frac{2}{3} = 50 \text{ torr}$$

44 Which of the following liquid pairs shows a positive deviation from Raoult's law? **[AIEEE 2004]**

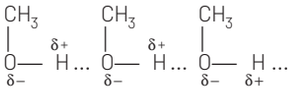
(a) Water — hydrochloric acid
(b) Benzene — methanol
(c) Water — nitric acid
(d) Acetone — chloroform

Ans. ***(b)***

Water and hydrochloric acid; and water and nitric acid form miscible solutions. They show negative deviation.

In case of CH_3COCH_3 and $CHCl_3$, there is interaction between them, thus force of attraction between CH_3COCH_3....$CHCl_3$ is larger than between $CHCl_3$....$CHCl_3$ or CH_3COCH_3....CH_3COCH_3 and thus, vapour pressure is less than expected—a negative deviation.

In case of CH_3OH, there is association by intermolecular H-bonding. When benzene is added to CH_3OH, H-bonding breaks and thus, force of attraction between CH_3OH and benzene molecule is smaller than between CH_3OH or benzene molecules (in pure state). Vapour pressure of mixture is greater than expected—a positive deviation.



45 If liquid *A* and *B* form an ideal solution, the **[AIEEE 2003]**

(a) enthalpy of mixing is zero
(b) entropy of mixing is zero
(c) free energy of mixing is zero
(d) free energy as well as the entropy of mixing are each zero

Ans. ***(a)***

For ideal solution, $\Delta H = 0$, $\Delta V = 0$;

$$F_{A-A} = F_{B-B} = F_{A-B}$$

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46 In a mixture of *A* and *B*, components show negative deviation when **[AIEEE 2002]**

(a) *A*—*B* interaction is stronger than *A*—*A* and *B*—*B* interaction
(b) *A*—*B* interaction is weaker than *A*—*A* and *B*—*B* interaction
(c) $\Delta V_{mix} > 0, \Delta S_{mix} > 0$
(d) $\Delta V_{mix} = 0, \Delta S_{mix} > 0$

Ans. ***(a)***

Negative deviation means lower vapour pressure. It suggests high boiling point, thus resultant intermolecular force should be stronger than individual one.

TOPIC 3
Colligative Properties

47 40 g of glucose (Molar mass = 180) is mixed with 200 mL of water. The freezing point of solution is ..... K. (Nearest integer)
[Given, $K_f = 1.86$ K kg mol^{-1}, density of water = 1.00 g cm^{-3}, freezing point of water = 273.15 K] **[2021, 27 Aug Shift-II]**

Ans. ***(271)***

40 g of glucose mixed with 200 mL of water
180 g of glucose = 1 moles of glucose
40 g of glucose mol = 0.22 mol
1 mL of water = 1 g of water
$[d = 1\text{ g/cm}^2, 1\text{ mL} = 1\text{ cm}^3]$
200 mL of water = 200 g of water
$\Delta T_f = K_f m$
where, ΔT_f = depression in freezing point,
K_f = molal elevation constant
= 1.86 K kg mol^{-1} and
m = molality of solution

$$\Delta T_f = \frac{1.86 \times 0.22}{200} \times 1000 \quad (\because 1000\text{ g} = 1\text{ kg})$$

$$\Delta T_f = 2\text{ K}$$

$$\therefore \quad (T_f - T_f') = 2$$

$[T_f$ = freezing point of water (273 K)
T_f' = freezing point of solution$]$

$$273\text{ K} - T_f' = 2\text{K}$$

$$T_f' = (273 - 2)\text{K} = 271\text{K}$$

48 1 kg of 0.75 molal aqueous solution of sucrose can be cooled up to −4°C before freezing. The amount of ice (in g) that will be separated out is ..... . (Nearest integer)
[Given, $K_f(H_2O) = 1.86$ K kg mol^{-1}] **[2021, 27 Aug Shift-I]**

Ans. ***(518)***

Let mass of water (initially present) = x g
Mass of sucrose = $(1000 - x)$ g

$$\text{Moles of sucrose} = \frac{1000 - x}{342}$$

$$\text{Molality} = \frac{\text{moles of sucrose}}{\text{mass of water (initially)}}$$

$$0.75 = \frac{\left(\frac{1000 - x}{342}\right)}{\left(\frac{x}{1000}\right)}$$

$$\frac{x}{1000} = \frac{1000 - x}{342 \times 0.75}$$

$$256.5x = 10^6 - 1000x$$

$$\Rightarrow \quad x = 795.86\text{ g}$$

Moles of sucrose = 0.5969
New mass of $H_2O = a$ kg
Depression in freezing point

$$\Delta T_f = K_f \times m$$

$$4 = \frac{0.5969}{a} \times 1.86$$

$$\Rightarrow \quad a = 0.2775\text{ kg}$$

Ice separated = 795.86 − 277.5
= 518.3 g ≈ 518 g.

49 1.46 g of a biopolymer dissolved in a 100 mL water at 300 K exerted an osmotic pressure of 2.42×10^{-3} bar. The molar mass of the biopolymer is ..... $\times 10^4$ g mol^{-1}. (Round off to the nearest integer)
[Use : $R = 0.083$ L bar mol^{-1} K^{-1}] **[2021, 27 July Shift-I]**

Ans. ***(15)***

Using formula; $\pi = CRT$
π = osmotic pressure,
C = molarity (concentration)
T = temperature of solution

$$\text{Molarity, } C = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}}$$

$$\text{Moles} = \frac{\text{Given mass}}{\text{Molecular mass}} = \frac{1.46}{M}$$

$$\text{Molarity} = \frac{1.46 \times 1000}{M \times 100\text{(mL)}} = \frac{1460}{100 \times M}$$

$$\therefore \quad \pi = \frac{1460}{100 \times M} \times 0.083 \times 300$$

Given, $\pi = 2.42 \times 10^{-3}$ bar
Therefore, $M = 15.02 \times 10^4$ g /mol

50 When 3.00 g of a substance '*X*' is dissolved in 100 g of CCl_4, it raises the boiling point by 0.60 K. The molar mass of the substance '*X*' is ..... g mol^{-1}. (Nearest integer)
[Given, K_b for CCl_4 is 5.0 K kg mol^{-1}] **[2021, 25 July Shift-II]**

Ans. ***(250)***

Weight of substance '*X*' = 3.00 g
Elevation in boiling point, $\Delta T_b = 0.60$
K_b (boiling constant) of CCl_4
= 5 K kg mol^{-1}

$$\text{Molality } (m) = \frac{\text{Weight of compound}}{\frac{\text{Molar mass of compound}}{\text{Volume of solution (in L)}}}$$

$$= \frac{\frac{3}{M}}{\frac{100}{1000}} \quad \ldots(i)$$

Formula, $\Delta T_b = K_b \times$ molality
Put value of (i) we get,

$$0.60 = 5 \times \frac{\frac{3}{M}}{\frac{100}{1000}} \Rightarrow 0.60 = 5 \times \frac{3 \times 1000}{M \times 100}$$

$$0.60\,M = 5 \times 30 \Rightarrow M = \frac{150}{0.60} = 250$$

∴ Molar mass of substance '*X*' is 250 g mol^{-1}.

51 Which one of the following 0.06 M aqueous solutions has lowest freezing point? **[2021, 22 July Shift-II]**

(a) $Al_2(SO_4)_3$ (b) $C_6H_{12}O_6$
(c) KI (d) K_2SO_4

Ans. ***(a)***

van't Hoff factor of $Al_2(SO_4)_3$ is 5 (maximum), so this will have lowest freezing point.
Depression in freezing point, $\Delta T_f = iK_f m$
where, i = van't Hoff factor
K_f = molal depression constant
m = molality
For freezing point to be lowest,
ΔT_f should be highest and the i values are follows

Solute	i
$C_6H_{12}O_6$	1
$Al_2(SO_4)_3$	5 → i highest, ΔT_f maximum, T_f minimum
KI	2
K_2SO_4	3

Hence, for $Al_3(SO_4)_3$ freezing point is lowest.

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52 A solute a dimerises in water. The boiling point of a 2 molar solution of *A* is 100.52°C.

The percentage association of *A* is ..... . (Round off to the nearest integer)

[Use : K_b for water $= 0.52\ \text{K kg mol}^{-1}$, boiling point of water = 100°C]

[2021, 18 March Shift-II]

Ans. ***(100)***

Given : $T_b = 100.52°\text{C}$

$T_b^\circ = 100°\text{C}$

$\Rightarrow \quad K_b = 0.52\ \text{K kg mol}^{-1}$

Elevation in boiling point,

$$\Delta T_b = T_b - T_b^\circ$$

$$\Delta T_b = 100.52 - 100$$

$$\Delta T_b = 0.52°\text{C}$$

For dimerisation (van't Hoff factor)

$$i = \left(1 - \frac{\alpha}{2}\right)$$

$\because \quad \Delta T_b = i \times K_b \times m$

$$0.52 = \left(1 - \frac{\alpha}{2}\right) \times 0.52 \times 2$$

$$\alpha = 1$$

So, percentage association = 100%

53 2 molal solution of a weak acid HA has a freezing point of 3.885°C. The degree of dissociation of this acid is ..... $\times 10^{-3}$. (Round off to the nearest integer).

[Given : Molal depression constant of water = $1.85\ \text{K kg mol}^{-1}$, freezing point of pure water = 0°C]

[2021, 18 March Shift-I]

Ans. ***(50)***

Given,

Depression in freezing point,

$$K_f = 1.85\ \text{K kg mol}^{-1}$$

$$T_f^\circ = 0°\text{C}$$

$$T_f = 3.885°\text{C}$$

$$\Delta T_f = T_f - T_f^\circ$$

$$= 3.885 - \text{C} = 3.885°\text{C}$$

$$\Delta T_f = 3.885°\text{C}$$

$$\Delta T_f = i \times K_f \times m$$

$$3.885 = i \times 1.85 \times 2$$

but, $\quad i = (1 + \alpha)$

$$3.885 = (1 + \alpha) \times 1.85 \times 2$$

$$\Rightarrow \quad \alpha = \frac{0.185}{3.7}$$

$$\Rightarrow \quad \alpha = 0.05$$

$$\alpha = 50 \times 10^{-3}$$

54 A 1 molal $K_4Fe(CN)_6$ solution has a degree of dissociation of 0.4. Its boiling point is equal to that of another solution which contains 18.1 weight per cent of a non-electrolytic solute *A*. The molar mass of *A* is ..... u. (Round off to the nearest integer).

[Density of water = $1.0\ \text{g cm}^{-3}$]

[2021, 17 March Shift-II]

Ans. ***(85)***

$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Initial conc.	1 m	0	0
Final conc.	(1 – 0.4) m = 0.6 m	4 × 0.4 = 1.6 m	0.4 m

Effective molality = 0.6 + 1.6 + 0.4 = 2.6 m

As elevation in boiling point is a colligative property which depends on the amount of solute. So, to have same boiling point, the molality of two solutions should be same.

Molality of non-electrolyte solution = molality of $K_4[Fe(CN)_6]$ = 2.6 m

Now, 18.1 weight per cent solution means 18.1 g solute is present in 100 g solution and hence, (100 – 18.1 =) 81.9 g water.

$$\text{Molality} = \frac{(\text{Mass of solute}/\text{Molar mass of solute})}{\text{Mass of solvent (g)}} \times 1000$$

$$\text{Now, } 2.6 = \frac{18.1/M}{81.9/1000}$$

where, *M* is the molar mass of non-electrolyte solute

Molar mass of solute, *M* = 85

55 C_6H_6 freezes at 5.5°C. The temperature at which a solution 10 g of C_4H_{10} in 200 g of C_6H_6 freeze is .....°C. (The molal freezing point depression constant of C_6H_6 is 5.12°C/m.) **[2021, 24 Feb Shift-II]**

Ans. ***(1)***

Pure solvent : $C_6H_6(l)$

Given, $\quad T_f^\circ = 5.5°\text{C}$

$$K_f = 5.12°$$

C/m $\Rightarrow \quad m = 200\ \text{g}$

$$m_{\text{solute}} = 10\ \text{g}$$

Molar mass of solute

$$C_4H_{10} = 12 \times 4 + 10 = 58$$

Solute (C_4H_{10}) is non-dissociative;

$\therefore \quad i = 1$

$\therefore \quad \Delta T_f = iK_f\, m$

$$\Rightarrow \quad (T_f^\circ - T_f^1) = 1 \times 5.12 \times \frac{(10/58)}{(200/1000)}$$

$$5.5 - T_f^1 = \frac{5.12 \times 5 \times 10}{58}$$

$$\Rightarrow \quad T_f^1 = 1.086°\text{C}$$

or $\quad T_f^1 \approx 1°\text{C}$

56 The size of a raw mango shrinks to a much smaller size when kept in a concentrated salt solution. Which one of the following processes can explain this? **[2020, 2 Sep Shift-II]**

(a) Osmosis

(b) Dialysis

(c) Diffusion

(d) Reverse osmosis

Ans. ***(a)***

When a raw mango is kept in a concentrated salt solution, the mango will shrink because of exo-osmosis. Mango cell membrane acts as semi-permeable membrane and its cell cytoplasm is considered as a solution of concentration, C_1M (say). Let, the concentration of salt solution is C_2M, where $C_1 < C_2$ (mentioned).

So, osmotic pressure developed at salt solution, π_2 will be greater than that at cell cytoplasm, π_1 at a given temperature.

$$\pi_1 = C_1RT$$

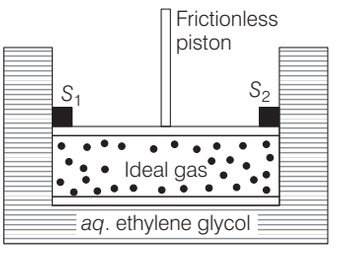
and $\quad \pi_2 = C_2RT$

So, solvent molecules (water) will flow out from mango cells to salt solution resulting shrinking of mango. This state is also known as plasmolysis.

57 A cylinder containing an ideal gas (0.1 mol of $1.0\ \text{dm}^3$) is in thermal equilibrium with a large volume of 0.5 molal aqueous solution of ethylene glycol at its freezing point. If the stoppers S_1 and S_2 (as shown in the figure) are suddenly withdrawn, the volume of the gas in litres after equilibrium is achieved will be .....

(Given, K_f (water) = $2.0\ \text{K kg mol}^{-1}$, $R = 0.08\ \text{dm}^3\ \text{atm K}^{-1}\text{mol}^{-1}$)

[2020, 9 Jan Shift-II]



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Ans. ***(2.18)***

$K_f = 2.0$ (Given) $m = 0.5$ m (Given)

$\Delta T_f = K_f \times m = 2 \times 0.5 = 1$

$\therefore$ T_f = Actual freezing point of water is –1.

$= 273 - 1 = 272$ K.

Pressure of gas after the stoppers are withdrawn = 1 atm (atmospheric pressure)

$\therefore \quad V = \dfrac{nRT}{p} = \dfrac{0.1 \times 0.08 \times 272}{1 \text{ atm}}$

$= 2.176 \text{ L} \approx 2.18 \text{ L}$

58 The osmotic pressure of a solution of NaCl is 0.10 atm and that of a glucose solution is 0.20 atm. The osmotic pressure of a solution formed by mixing 1 L of the sodium chloride solution with 2 L of the glucose solution is $x \times 10^{-3}$ atm. x is ..... (nearest integer).

[2020, 4 Sep Shift-II]

Ans. ***(167)***

Osmotic pressure, $\pi = i \times C \times RT$

Here, i = van't Hoff factor,

T = temperature

C = concentration and

R = gas constant.

For NaCl, $i = 2$

So, $\pi_{NaCl} = i \times C_{NaCl} \times RT$

$0.1 = 2 \times C_{NaCl} \times RT$

$C_{NaCl} = \dfrac{0.05}{RT}$

For glucose, $i = 1$ because it cannot ionise

So, $\pi_{glucose} = i \times C_{glucose} \times RT$

$0.2 = 1 \times C_{glucose} \times RT$

$C_{glucose} = \dfrac{0.2}{RT}$

($\because$ n_{NaCl} = numbers of moles NaCl)

n_{NaCl} in 1 L $= C_{NaCl} \times V_{litre}$

$= \dfrac{0.05}{RT}$ ($n_{glucose}$ = number of moles of glucose)

$n_{glucose}$ in 2 L $= C_{glucose} \times V_{litre} = \dfrac{0.4}{RT}$

$V_{total} = 1 + 2 = 3$ L

So, final conc. NaCl $= \dfrac{0.05}{3RT}$

Final conc. glucose $= \dfrac{0.4}{3RT}$

$\pi_{total} = \pi_{NaCl} + \pi_{glucose}$

$= [i \times C_{NaCl} + C_{glucose}]\, RT$

$= \left(\dfrac{2 \times 0.05}{3RT} + \dfrac{0.4}{3RT}\right) \times RT = \dfrac{0.5}{3}$ atm

$= 0.1666$ atm $= 166.6 \times 10^{-3}$ atm

$= 167.00 \times 10^{-3}$ atm

So, $x = 167.00$

59 A set of solutions is prepared using 180 g of water as a solvent and 10 g of different non-volatile solutes A, B and C. The relative lowering of vapour pressure in the presence of these solutes are in the order

[Given, molar mass of $A = 100$ g mol^{-1}; $B = 200$ g mol^{-1}; $C = 10{,}000$ g mol^{-1}]

[2020, 6 Sep Shift-II]

(a) $B > C > A$ (b) $C > B > A$

(c) $A > B > C$ (d) $A > C > B$

Ans. ***(c)***

Relative lowering in vapour pressure

$$(\text{RLVP}) = \frac{p^\circ - p_S}{p^\circ} = \chi_{\text{solute}} \text{ or RLVP} = \frac{\Delta p}{p^\circ} = \chi_{\text{solute}}$$

$n \rightarrow$ moles of solute $= \dfrac{w}{M}$;

$N \rightarrow$ moles of solvent $= \dfrac{w}{M}$

Given, weight of solvent (water) = 180 g

Weight of different non-volatile solute w_A, w_B and $w_C = 10$

Molar mass of $M_A = 100$ g mol^{-1}

$M_B = 200$ g mol^{-1}

$\Rightarrow$ $M_C = 10{,}000$ g mol^{-1}

RLVP for A,

$$\left(\frac{\Delta p}{p^\circ}\right)_A = \frac{\frac{10}{100}}{\frac{10}{100} + \frac{180}{18}} = \frac{0.1}{1.1} = 0.091$$

RLVP for B,

$$\left(\frac{\Delta p}{p^\circ}\right)_B = \frac{\frac{10}{200}}{\frac{10}{200} + \frac{180}{18}} = \frac{0.05}{10.05} = 0.0049$$

RLVP for C,

$$\left(\frac{\Delta p}{p^\circ}\right)_C = \frac{\frac{10}{10{,}000}}{\frac{10}{10{,}000} + \frac{180}{18}} = \frac{0.001}{0.001 + 10} = \frac{0.001}{10.001} = 0.000099$$

From the above value the relative lowering of vapour pressure in the presence of there solute are in the following order :

$$\left(\frac{\Delta p}{p^\circ}\right)_A > \left(\frac{\Delta p}{p^\circ}\right)_B > \left(\frac{\Delta p}{p^\circ}\right)_C$$

Hence, option (c) is correct.

60 1 g of a non-volatile, non-electrolyte solute is dissolved in 100 g of two different solvents A and B, whose ebullisocopic constants are in the ratio of 1 : 5. The ratio of the elevation in their boiling points, $\dfrac{\Delta T_b(A)}{\Delta T_b(B)}$, is

[2019, 10 April Shift-II]

(a) 5 : 1 (b) 10 : 1 (c) 1 : 5 (d) 1 : 0.2

Ans. ***(c)***

The expression of elevation of boiling point,

$$\Delta T_b = K_b \times m \times i = k_b \times \frac{w_2 \times 1000}{M_2 \times w_1} \times i$$

where, m = molality

i = van't Hoff factor = 1 (for non-electrolyte/non-associable)

w_2 = mass of solute in g = 1 g (present in both of the solutions)

M_2 = molar mass of solute in g mol^{-1} (same solute in both of the solutions)

w_1 = mass of solvent in g = 100 g (for both of the solvents A and B)

K_b = ebullioscopic constant

So, the expression becomes,

$$\Delta T_b \propto K_b$$

$$\Rightarrow \frac{\Delta T_b(A)}{\Delta T_b(B)} = \frac{K_b(A)}{K_b(B)} = \frac{1}{5} \left[\text{Given } \frac{K_b(A)}{K_b(B)} = \frac{1}{5}\right]$$

61 At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mm Hg, lowering of vapour pressure will be (Molar mass of urea = 60 g mol^{-1})

[2019, 10 April Shift-I]

(a) 0.027 mmHg (b) 0.031 mmHg

(c) 0.017 mmHg (d) 0.028 mmHg

Ans. ***(c)***

Key Idea For dilute solution, lowering of vapour pressure (Δp) = $p^\circ - p$ and relative lowering of vapour pressure = $\dfrac{\Delta p}{p^\circ}$ which is a colligative property of solutions.

$$\frac{\Delta p}{p^\circ} = \chi_B \times i \Rightarrow \Delta p = \chi_B \times i \times p^\circ$$

where, p° = vapour pressure of pure solvent

i = van't Hoff factor

χ_B = mole fraction of solute

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Given,

$p°$ = vapour pressure of pure water of 25°C = 35 mm Hg

χ_B = mole fraction of solute (urea)

$$= \frac{n_B}{n_A + n_B} = \frac{\frac{0.60}{60}}{\frac{360}{18} + \frac{0.60}{60}} = \frac{0.01}{20 + 0.01}$$

$$= \frac{0.01}{20.01} = 0.0005$$

i = van't Hoff factor = 1 (for urea)

Now, according to Raoult's law,

$$\Delta p = \chi_B \times i \times p°$$

On substituting the above given values, we get

$$\Delta p = 0.0005 \times 1 \times 35 = 0.0175 \text{ mm Hg}$$

62 A solution is prepared by dissolving 0.6 g of urea (molar mass = 60 g mol^{-1}) and 1.8 g of glucose (molar mass = 180 g mol^{-1}) in 100 mL of water at 27°C. The osmotic pressure of the solution is ($R = 0.08206$ L atm K^{-1} mol^{-1})

[2019, 12 April Shift-II]

(a) 8.2 atm (b) 2.46 atm
(c) 4.92 atm (d) 1.64 atm

Ans. *(c)*

Key Idea Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature (T).

Thus, $\pi \propto C$, $\pi = CRT$ (for dilute solution)

$$\pi = \frac{n}{V}RT$$

For the relation, $\pi = CRT = \frac{n}{V}RT$

Given, mass of urea = 0.6 g

Molar mass of urea = 60 g mol^{-1}

Mass of glucose = 1.8 g

Molar mass of glucose = 180 g mol^{-1}

$$\pi = \frac{[n_2\,(\text{urea}) + n_2(\text{glucose})]}{V}RT$$

$$= \frac{\left(\frac{0.6}{60} + \frac{1.8}{180}\right)}{100} \times 1000 \times 0.0821 \times 300$$

$$= (0.01 + 0.01) \times 10 \times 0.0821 \times 300$$

$$\pi = 4.92 \text{ atm}$$

63 Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is

(a) $K_b = 1.5\,K_f$ (b) $K_b = 0.5\,K_f$
(c) $K_b = K_f$ (d) $K_b = 2K_f$

[2019, 10 Jan Shift-II]

Ans. *(d)*

Elevation in boiling point

$$(\Delta T_b) = K_b \times m \times i$$

Depression is freezing point

$$(\Delta T_f) = K_f \times m \times i$$

where, m = molality

For the glucose solution (van't Hoff factor, $i = 1$),

$$\Delta T_b^{1m} = \Delta T_f^{2m} = 2K$$

So, $K_b \times 1 \times 1 = K_f \times 2 \times 1$

$\Rightarrow$ $K_b = 2K_f$

64 Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous solution of Y. If molecular weight of X is A, then molecular weight of Y is

(a) 4A (b) 2A
(c) 3A (d) A

[2019, 12 Jan Shift-I]

Ans. *(c)*

Given, Freezing point of 4% aqueous solution of X.

= Freezing point of 12% aqueous solution of Y

or $(\Delta T_f)_X = (\Delta T_f)_Y$ $[\because \Delta T_f = T_f° - T_f]$

$K_f \times m_X = K_f m_Y$

where, m_X and m_Y are molality of X and Y, respectively.

or $m_X = m_Y$

Now,

$$\text{molality} = \frac{\text{Number of moles of solute } (n)}{\text{Mass of solvent (in kg)}}$$

$$n = \frac{\text{Weight}}{\text{Molecular mass}}$$

$$\frac{w_X}{M_X \times (w_{\text{solvent}})_1} = \frac{w_Y}{M_Y \times (w_{\text{solvent}})_2}$$

Given, $w_X = 4$ and $w_{\text{solvent})_1} = 96$

$w_Y = 12$ and $w_{(\text{solvent})_2} = 88$

$M_X = A$

$$\therefore \quad \frac{4 \times 1000}{M_X \times 96} = \frac{12 \times 1000}{M_Y \times 88}$$

Thus, $M_Y = \frac{12 \times 1000 \times M_X \times 96}{4 \times 1000 \times 88}$

$$= \frac{96 \times 12}{4 \times 88} \times A$$

$$= 3.27A \approx 3\,A$$

65 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is **[JEE Main 2016]**

(a) 76.0 (b) 752.4
(c) 759.0 (d) 7.6

Ans. *(b)*

Vapour pressure of water ($p°$) = 760 torr

Number of moles of glucose

$$= \frac{\text{Mass (g)}}{\text{Molecular mass (g mol}^{-1})}$$

$$= \frac{18 \text{ g}}{180 \text{ gmol}^{-1}} = 0.1 \text{ mol}$$

Molar mass of water = 18 g/mol

Mass of water (given) = 178.2g

Number of moles of water

$$= \frac{\text{Mass of water}}{\text{Molar mass of water}}$$

$$= \frac{178.2 \text{ g}}{18 \text{ g/mol}} = 9.9 \text{ mol}$$

Total number of moles = (0.1 + 9.9) moles = 10 moles

Now, mole fraction of glucose in solution = Change in pressure with respect to initial pressure

i.e. $\frac{\Delta p}{p°} = \frac{0.1}{10}$

or $\Delta p = 0.01p° = 0.01 \times 760 = 7.6$ torr

$\therefore$ Vapour pressure of solution

= (760 – 7.6) torr

= 752.4 torr

66 The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is

[JEE Main 2015]

(a) 32 (b) 64
(c) 128 (d) 488

Ans. *(b)*

Given, p_o = 185 torr at 20° C

p_s = 183 torr at 20° C

Mass of non-volatile substance, m = 1.2 g

Mass of acetone taken = 100 g

M = ?

As , we have

$$\frac{p_o - p_s}{p_s} = \frac{n}{N}$$

Putting the values, we get,

$$\frac{185 - 183}{183} = \frac{\frac{1.2}{M}}{\frac{100}{58}}$$

$$\Rightarrow \quad \frac{2}{183} = \frac{1.2 \times 58}{100 \times M}$$

$$\therefore \quad M = \frac{183 \times 1.2 \times 58}{2 \times 100}$$

$$M = 63.684 \approx 64 \text{ g / mol}$$

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67 K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, then how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8°C? **[AIEEE 2012]**

(a) 72 g (b) 93 g
(c) 39 g (d) 27 g

Ans. ***(b)***

Coolant is glycol ($C_2H_6O_2$) and it is non-electrolyte.

$$\Delta T_f = 2.8°\,C \Rightarrow \Delta T_f = \frac{1000 K_f w_1}{m_1 w_2}$$

$$2.8 = \frac{1000 \times 1.86 \times w_1}{62 \times 1000}$$

$$\Rightarrow \quad w_1 = 93.33 \text{ g}$$

68 Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at –6° C will be (K_f for water = 1.86 K kg mol^{-1} and molar mass of ethylene glycol = 62 g mol^{-1}) **[AIEEE 2011]**

(a) 804.32 g (b) 204.30 g
(c) 400.00 g (d) 304.60 g

Ans. ***(a)***

ΔT_f = Freezing point of H_2O – freezing point of ethylene glycol solution

$= 0 - (-6°) = 6°$

$K_f = 1.86°$ K kg mol^{-1}

w_1 = Mass of ethylene glycol in grams

w_2 = Mass of solvent (H_2O) in grams

$= 4000$ g

m_1 = Molar mass of ethylene glycol

$= 62$ g mol^{-1}

$$\Delta T_f = \frac{1000\, K_f\, w_1}{m_1\, w_2} \Rightarrow 6 = \frac{1000 \times 1.86 \times w_1}{62 \times 4000}$$

$$w_1 = 804.32 \text{ g}$$

69 The vapour pressure of water at 20°C is 17.5 mmHg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be **[AIEEE 2008]**

(a) 17.675 mmHg (b) 15.750 mmHg
(c) 16.500 mmHg (d) 17.325 mmHg

Ans. ***(d)***

This problem is related to the relative lowering of vapour pressure as glucose is a non-volatile solute. Thus, according to Raoult's law,

$$\frac{p^0 - p_{\text{solute}}}{p^0} = X_{\text{solute}}$$

$$\text{Moles of glucose} = \frac{18}{180} = 0.1$$

$$\text{Moles of } H_2O = \frac{178.2}{18} = 9.9$$

$$X_{\text{glucose}} = \frac{0.1}{9.9 + 0.1} = \frac{0.1}{10}$$

Thus, $\quad \dfrac{17.5 - p_s}{17.5} = \dfrac{0.1}{10}$

So, $\quad p_s = 17.325$ mm Hg

70 A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3}, molar mass of the substance will be **[AIEEE 2007]**

(a) 90.0 g mol^{-1} (b) 115.0 g mol^{-1}
(c) 105.0 g mol^{-1} (d) 210.0 g mol^{-1}

Ans. ***(d)***

Osmotic pressure of isotonic solutions are equal.

Therefore, $\pi_1 = \pi_2$

$$\Rightarrow \quad C_1 RT = C_2 RT \quad \Rightarrow \quad C_1 = C_2$$

If densities of both the solutions are equal, then 5.25 g of a substance and 1.5 g of urea are dissolved in the same volume of the solvent, thus,

$$C_1 = \frac{5.25/M}{V}$$

[$\because M$ = molecular weight of unknown substance]

$$C_2 = \frac{5.25/60}{V}$$

$$\therefore \quad \frac{5.25/M}{V} = \frac{1.5/60}{V} \Rightarrow M = 210.0 \text{ g mol}^{-1}$$

71 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is **[AIEEE 2006]**

(a) 759.00 torr (b) 7.60 torr
(c) 76.00 torr (d) 752.40 torr

Ans. ***(d)***

According to Raoult's law, relative lowering of vapour pressure,

$$\frac{p° - p_s}{p°} = \frac{n}{N}$$

$$\frac{760 - p_s}{760} = \frac{18/180}{18/180 + 178.2/18}$$

$$\frac{760 - p_s}{760} = \frac{0.1}{10}$$

$$\Rightarrow \quad p_s = 760 - 7.6 = 752.40 \text{ torr}$$

72 Equimolar solutions in the same solvent have **[AIEEE 2005]**

(a) different boiling point and different freezing point
(b) same boiling point and same freezing point
(c) same freezing point but different boiling point
(d) same boiling point but different freezing point

Ans. ***(b)***

Boiling point and freezing point depend on K_b (molal elevation constant) and K_f (molal depression constant) of the solvent. Thus, equimolar solution (of the non-electrolyte), will have same boiling point and also same freezing point.

$\Delta T_f = K_f \times$ molality;

$\Delta T_b = K_b \times$ molality

Note In this question, nature of solute has not been mentioned. Hence, we have assumed that solute is non-electrolyte.

73 A pressure cooker reduces cooking time for food because **[AIEEE 2003]**

(a) heat is more evenly distributed in the cooking space
(b) boiling point of water involved in cooking is increased
(c) the higher pressure inside the cooker crushes the food material
(d) cooking involves chemical changes helped by a rise in temperature

Ans. ***(b)***

Higher pressure inside the cooker increases boiling point, thus heat consistently given is used up by food material instead in boiling and constant boiling evaporation.

74 For an aqueous solution, freezing point is – 0.186°C. Elevation of the boiling point of the same solution is ($K_f = 1.86°$ mol^{-1} kg and $K_b = 0.512°$ mol^{-1} kg) **[AIEEE 2002]**

(a) 0.186° (b) 0.0512°
(c) 1.86° (d) 5.12°

Ans. ***(b)***

We know that, $\Delta T_b = mK_b$, $\Delta T_f = mK_f$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} = \frac{0.512}{1.86}$$

$$\Delta T_b = \frac{0.512}{1.86} \times 0.186 = 0.0512°$$

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TOPIC 4
Abnormal Molecular Masses and Distribution Law

75 1.22 g of an organic acid is separately dissolved in 100 g of benzene (K_b = 2.6 K kg mol^{-1}) and 100 g of acetone (K_b = 1.7 K kg mol^{-1}). The acid is known to dimerise in benzene but remain as a monomer in acetone. The boiling point of the solution in acetone increases by 0.17°C. The increase in boiling point of solution in benzene in °C is $x \times 10^{-2}$. The value of x is ..... (Nearest integer)
[Atomic mass : C = 12.0, H = 1.0, O= 16.0] **[2021, 31 Aug Shift-II]**

Ans. ***(13)***

With benzene as solvent, *R*COOH dimerises.

$$2R\text{COOH} \rightleftharpoons (R\text{COOH})_2$$

$$\therefore \quad i = \frac{1}{2}$$

$$\Delta T_b = i \times K_b \times m$$

where, ΔT_b = boiling point elevation,
K_b = ebulliscopic constant
m = molality
i = van't Hoff factor

$$\Delta T_b = \frac{1}{2} \times 2.6 \times \frac{1.22/M_w}{100/1000} \quad \ldots(i)$$

With acetone as solvent, no dimerisation.

$$\therefore \quad i = 1$$

$$\Delta T_b = i \times K_b \times m$$

$$0.17 = 1 \times 1.7 \times \frac{1.22/M_w}{100/1000} \quad \ldots(ii)$$

Eq. (i) divide by Eq. (ii),

$$\frac{\Delta T_b}{0.17} = \frac{\frac{1}{2} \times 2.6 \times \frac{1.22/M_w}{100/1000}}{1 \times 1.7 \times \frac{1.22/M_w}{100/1000}}$$

$$\Rightarrow \quad \Delta T_b = \frac{0.26}{2} = 13 \times 10^{-2}$$

$$x = 13$$

76 Which one of the following 0.10 M aqueous solutions will exhibit the largest freezing point depression ? **[2021, 31 Aug Shift-I]**

(a) Hydrazine (b) Glucose
(c) Glycine (d) $KHSO_4$

Ans. ***(d)***

The van't Hoff factor (i) is highest for $KHSO_4$ as it dissociate into its ions. van't Hoff factor is the ratio of total number of ions produced after complete dissociation to before dissociation. Hydrazine, glucose and glycine will not dissociate to produce ions.

Whereas, $KHSO_4$ dissociates into ions.

$$KHSO_4 \longrightarrow K^+ + HSO_4^-$$

Hence, i will highest for $KHSO_4$

$\therefore$ Colligative property i.e. freezing point depression will be highest for $KHSO_4$ as $\Delta T_f \propto i$ [$\because m$ is constant i.e. 0.1]

Hence, correct option is (d).

77 In a solvent 50% of an acid H*A* dimerises and the rest dissociates. The van't Hoff factor of the acid is ..... $\times 10^{-2}$.
(Round off to the nearest integer) **[2021, 27 July Shift-II]**

Ans. ***(125)***

1 mole of acid H*A*.

Dimerisation $2HA \rightleftharpoons H_2A_2$

Initial	0.5	0
Final	0	0.25

Dissociation

$$HA \rightleftharpoons H^+ + A^-$$

Initial	0.5	0	0
Final	0	0.5	0.5

$$\text{van't Hoff factor } (i) = \frac{\text{Final moles}}{\text{Initial moles}}$$

$$= \frac{0.25 + 0.5 + 0.5}{1}$$

$$= 1.25 = 125 \times 10^{-2}$$

78 83 g of ethylene glycol dissolved in 625 g of water. The freezing point of the solution is .....K. (Nearest integer)
[Use, molal freezing point depression constant of water = 1.86 K kg mol^{-1},
Freezing point of water = 273 K and Atomic masses : C = 12.0 u, O = 16.0 u, H = 1.0 u] **[2021, 26 Aug Shift-II]**

Ans. ***(269)***

$$\Delta T_f = iK_f \times m$$

For ethylene glycol, $i = 1$

$$\text{Molality } (m) = \frac{\text{Number of moles of solute}}{\text{Weight of solvent (kg)}}$$

$$\Delta T_f = 1 \times 1.86 \times \frac{83 \times 1000}{62 \times 625} \simeq 3.98$$

Freezing point of solution = Freezing point – ΔT_f of water
= 273 – 3.98 ≃ 269.

79 Of the following four aqueous solutions, total number of those solutions whose freezing point is lower than that of 0.10 M C_2H_5OH is ..... . (Integer answer)
(i) 0.10 M $Ba_3(PO_4)_2$
(ii) 0.10 M Na_2SO_4
(iii) 0.10 M KCl
(iv) 0.10 M Li_3PO_4 **[2021, 26 Aug Shift-I]**

Ans. ***(4)***

As 0.10 M C_2H_5OH is non-dissociative in nature and all salts [0.10 M $Ba_3(PO_4)_2$, 0.10 M Na_2SO_4, 0.10 M KCl, 0.10 M Li_3PO_4] are electrolyte and dissociative in nature.

$$\Delta T_f = iK_f m$$

Where i is van't Hoff factor.

$i = 1$ for C_2H_5OH (no dissociation)

$i > 1$ for all other electrolytes where dissociation takes place.

So, for all these electrolytes effective molarity is more than 0.10. So, all the elecrolytes given will have low freezing point.

80 The water having more dissolved O_2 is **[2021, 22 July Shift-II]**

(a) boiling water (b) water at 80°C
(c) polluted water (d) water at 4° C

Ans. ***(d)***

At 4°C, the water have more dissolved O_2. Since, dissolution of O_2 gas in water is an exothermic process, and solubility of oxygen in water is high, at lower temperature. On increasing temperature, solubility of gas decreases and water pollution also decrease the solubility. First, the solubility of oxygen increases as temperature decreases i.e. warmer surface water requires less dissolved oxygen to reach 100% air saturation than cooler water.

81 When 12.2 g of benzoic acid is dissolved in 100 g of water, the freezing point of solution was found to be – 0.93°C ($K_f(H_2O)$ = 1.86 K kg mol^{-1}). The number (n) of benzoic acid molecules associated (assuming 100% association) is ..... . **[2021, 26 Feb Shift-II]**

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Ans. *(2)*

$$n\,\underset{\text{Benzoic acid}}{\text{PhCOOH}} \xrightarrow{\text{Association}} (\text{PhCOOH})_n$$

Assuming 100% association ($\alpha = 1$),

$$\Rightarrow \quad i = 1-\alpha\left(1-\frac{1}{n}\right)=\frac{1}{n} \qquad [\because \alpha = 1]$$

Now, $\Delta T_f = K_f \times m \times i$

$$0-(0.93) = 1.86\times\frac{w_B\times 1000}{w_A\times M_B}\times\frac{1}{n}$$

$[\because w_B$ = mass of PhCOOH = 12.2 g
w_A = mass of H_2O = 100 g
M_B = molar mass of PhCOOH$]$

$$= 122\,\text{g mol}^{-1}$$

$$= 1.86\times\frac{12.2\times 1000}{100\times 122}\times\frac{1}{n}$$

$$\Rightarrow \quad n=\frac{1.86\times 12.2\times 1000}{0.93\times 100\times 122}=2$$

$\therefore$ Number of benzoic acid molecules associated, $n = 2$

82 If a compound *AB* dissociates to the extent of 75% in an aqueous solution, the molality of the solution which shows a 2.5 K rise in the boiling point of the solution is ..... molal. (Rounded off to the nearest integer)

$[K_b = 0.52\ \text{K kg mol}^{-1}]$

[2021, 25 Feb Shift-II]

Ans. *(3)*

As *AB* is a binary electrolyte,

$\therefore \quad AB \rightleftharpoons A^+ + B^-,\ n = 2$

$$i = 1+\alpha(n-1) = 1+\frac{75}{100}(2-1) = 1.75$$

Given, $\Delta T_b = 2.5$ K

$K_b = 0.52\ \text{K kg mol}^{-1}$

$\therefore \quad \Delta T_b = K_b \times m \times i$

$$\Rightarrow \quad m=\frac{\Delta T_b}{K_b\times i}=\frac{2.5}{0.52\times 1.75}$$

$$= 2.74 \simeq 3\ \text{mol/kg}$$

83 1 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is ..... K (Rounded off to the nearest integer). [Given, K_b for $(H_2O) = 0.52\ \text{K kg mol}^{-1}$]

[2021, 25 Feb Shift-I]

Ans. *(375)*

Given, $K_b(H_2O) = 0.52\ \text{K kg mol}^{-1}$

$$A_2B_3 \longrightarrow 2A^{+3} + 3B^{-2}$$

No. of ions, $n = 5$, concentration, $m = 1$ molal (Given)

$$\alpha = \frac{60}{100} = 0.6$$

$$\Delta T_b = i\cdot K_f \cdot m$$

$$= [(1+(n-1)\alpha]\times K_f \times m$$

$$\Delta T_b = [(1+(5-1)0.6]\times 0.52\times 1$$

$$= (1+2.4)\times 0.52$$

$$\Delta T_b = 1.768$$

$$T_b = 1.768 + 373.15$$

$$= 374.91 = 375\ \text{K}$$

84 The elevation of boiling point of 0.10 m aqueous $CrCl_3 \cdot xNH_3$ solution is two times that of 0.05 m aqueous $CaCl_2$ solution. The value of *x* is ..... .

[Assume 100% ionisation of the complex and $CaCl_2$, coordination number of Cr as 6, and that all NH_3 molecules are present inside the coordination sphere]

[2020, 6 Sep Shift-I]

Ans. *(5.00)*

$$\Delta T_b = i \times m \times K_b$$

For $CaCl_2$, $i = 3$, $m_{(CaCl_2)} = 0.05$ m

$\therefore \quad \Delta T_b = 3\times 0.05\times K_b = 0.15K_b$

Molality of $CrCl_3\cdot xNH_3 = 0.1$ m

$\therefore \quad \Delta T_b' = i\times m\times K_b = 0.1iK_b$

Given that : $0.1iK_b = 2\times 0.15\times K_b$

$\therefore i = 3$ and coordination number is 6.

Thus, complex will be $[Cr(NH_3)_5Cl]Cl_2$

$\therefore \quad x = 5$

Hence, the correct answer is 5.

85 How much amount of NaCl should be added to 600 g of water ($\rho = 1.00$ g/mL) to decrease the freezing point of water to –0.2°C? ..... (The freezing point depression constant for water = 2 K kg mol^{-1})

[2020, 9 Jan Shift-I]

Ans. *(1.76)*

$$\Delta T_f = i\times m\times K_f = \frac{i\times K_f \times w_{NaCl}\times 1000}{\underset{(=58.5)}{M_{NaCl}}\times w_{H_2O}}$$

$$(m = \text{molality}) = \frac{w_B\times 1000}{M_B\times w_A}$$

$\Delta T_f = 0.2$ because freezing point $= -0.2$°C

K_f of water 2 K kg mol^{-1} (Given)

i = van't Hoff factor, for NaCl = 2

$$\therefore w_{NaCl} = \frac{\Delta T_f \times M_{NaCl}\times w_{H_2O}}{i\times K_f\times 1000}$$

$$= \frac{0.2\times 58.5\times 600}{2\times 2\times 1000} = 1.755\ \text{g} \simeq 1.76\ \text{g}$$

86 The osmotic pressure of a dilute solution of an ionic compound *XY* in water is four times that of a solution of 0.01 M $BaCl_2$ in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of *XY* (in mol L^{-1}) in solution is

[2019, 9 April Shift-I]

(a) 4×10^{-2} (b) 16×10^{-4}
(c) 4×10^{-4} (d) 6×10^{-2}

Ans. *(d)*

Key Idea Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature, $\pi = CRT$

Concentration of $BaCl_2 = 0.01$ M (Given)

$\pi_{XY} = 4\pi_{BaCl_2}$ (Given)

$i\times CRT = 4\times i\times CRT$ ...(i)

For the calculation of i,

$XY \longrightarrow X^+ + Y^-$ (Here, $i = 2$)

$BaCl_2 \longrightarrow Ba^{2+} + 2Cl^-$ (Here, $i = 3$)

Putting the values of i in (i)

$$2\times[XY] = 4\times 3\times[BaCl_2]$$

$$2\times[XY] = 12\times 0.01$$

$$[XY] = \frac{12\times 0.01}{2}$$

So, the concentration of *XY*

$$= 0.06\ \text{mol L}^{-1}$$

$$= 6\times 10^{-2}\ \text{mol L}^{-1}$$

87 Molal depression constant for a solvent is 4.0 K kg mol^{-1}. The depression in the freezing point of the solvent for 0.03 mol kg^{-1} solution of K_2SO_4 is (Assume complete dissociation of the electrolyte) **[2019, 9 April Shift-II]**

(a) 0.18 K (b) 0.36 K
(c) 0.12 K (d) 0.24 K

Ans. *(b)*

Key Idea Depression in freezing point (ΔT_f) is given by $\Delta T_f = iK_f m$

i = vant Hoff factor
K_f = molal depression constant
m = molality

$K_f = 4.0\ \text{K kg mol}^{-1}$ (Given)

$m = 0.03\ \text{mol kg}^{-1}$ (Given)

$\Delta T_f = ?$

For K_2SO_4, $i = 3$

It can be verified by the following equation :

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$$

Using formula

$\Delta T_f = iK_f \times m$

$= 3\times 4\times 0.03 = 0.36$ K

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88 A solution contain 62 g of ethylene glycol in 250 g of water is cooled upto –10°C. If K_f for water is 1.86 K kg mol^{-1}, then amount of water (in g) separated as ice is

[2019, 9 Jan Shift-II]

(a) 32 (b) 48 (c) 64 (d) 16

Ans. ***(c)***

Considering the expression of the depression in freezing point of a solution,

$$\Delta T_f = K_f \times m \times i$$

$$T_f^\circ - T_f = K_f \times \frac{w_B \times 1000}{M_B \times w_A(\text{in g})} \times i \quad \ldots(i)$$

Here, $T_f^\circ = 0°C$, $T_f = -10°C$

w_B = mass of ethylene glycol = 62 g

M_B = molar mass of ethylene glycol

$$\left(\begin{array}{l} CH_2—CH_2 \\ | \quad\quad | \\ OH \quad\; OH \end{array}\right)$$

$= 62 \text{ g mol}^{-1}$

w_A = mass of water in g as liquid solvent,

i = van't-Hoff factor = 1

(for ethylene glycol in water)

$K_f = 1.86 \text{ K kg mol}^{-1}$

On substituting in Eq. (i), we get

$$0 - (-10) = 1.86 \times \frac{62 \times 1000}{62 \times w_A} \times 1$$

$$\Rightarrow \quad w_A = \frac{1.86 \times 62 \times 1000}{10 \times 62}$$

$$= 186 \text{ g}$$

So, amount of water separated as ice (solid solvent)

$$= 250 - w_A = (250 - 186) \text{ g} = 64 \text{ g}$$

89 The freezing point of a diluted milk sample is found to be –0.2° C, while it should have been –0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample?

(a) 2 cups of water to 3 cups of pure milk
(b) 1 cup of water to 3 cups of pure milk
(c) 3 cups of water to 2 cups of pure milk
(d) 1 cup of water to 2 cups of pure milk

[2019, 11 Jan Shift-I]

Ans. ***(c)***

We know that,

Depression in freezing points (ΔT_f)

$$T^\circ_f - T_f = K_f \times m \times i$$

where, K_f = molal depression constant

$$m = \text{molality} = \frac{w_{\text{solute}} \times 1000}{M_{\text{solute}} \times w_{\text{solvent (in g)}}}$$

i = van't Hoff factor

For diluted milk

$$\Delta T_{f_1} = K_f \times m_1 \times i$$

$$\Rightarrow 0 - (0.2) \Rightarrow 0.2 = K_f \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_1(H_2O)} \times 1$$

For pure milk

$$\Delta T_{f_2} = K_f \times m_2 \times i$$

$$\Rightarrow 0 - (-0.5) = 0.5 = K_f \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_2(H_2O)} \times 1$$

So, $$\frac{0.2}{0.5} = \frac{K_f}{K_f} \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_1(H_2O)} \times \frac{M_{\text{milk}} \times w_2(H_2O)}{w_{\text{milk}} \times 1000}$$

$$= \frac{w_2(H_2O)}{w_1(H_2O)}$$

$$\Rightarrow \quad \frac{w_2\,(H_2O)(\text{in pure milk})}{w_1\,(H_2O)(\text{in diluted milk})} = \frac{2}{5}$$

i.e. 3 cups of water has to be added to 2 cups of pure milk.

90 K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is **[2019, 11 Jan Shift-II]**

(a) 1.6 (b) 1.8
(c) 2.2 (d) 2.0

Ans. ***(b)***

The ionisation of K_2HgI_4 in aqueous solution is as follows:

$$K_2[HgI_4] \rightleftharpoons 2K^+ + [HgI_4]^{2-}$$

van't Hoff factor (i) for ionisation reaction is given as, $i = 1 + \alpha(n - 1)$

where, n = number of ions,

α = degree of ionisation or dissociation

From above equation, it is clear that $n = 3$

$$i = 1 + 0.4\,(3 - 1)$$

[Given, $\% \alpha = 40\%$ or $\alpha = 0.4$] = 1.8

91 Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is

(Given that $K_f = 5 \text{ K kg mol}^{-1}$, molar mass of benzoic acid = 122 g mol^{-1})

[2019, 12 Jan Shift-II]

(a) 1.8 g (b) 1.0 g (c) 2.4 g (d) 1.5 g

Ans. ***(c)***

Molecules of benzoic acid dimerise in benzene as:

$$2(C_6H_5COOH) \rightleftharpoons (C_6H_5COOH)_2$$

Now, we know that depression in freezing point (ΔT_f) is given by following equation:

$$\Delta T_f = i \times K_f \times m = \frac{i \times K_f \times w_{\text{solute}} \times 1000}{Mw_{\text{solute}} \times w_{\text{solvent}}} \quad \ldots(i)$$

Given, w_{solute} (benzoic acid) = w g

w_{solvent} (benzene) = 30 g

Mw_{solute} (benzoic acid) = 122 g mol^{-1},

$\Delta T_f = 2$ K

$K_f = 5 \text{ K kg mol}^{-1}$, $\% \alpha = 80$ or $\alpha = 0.8$

$$2(C_6H_5COOH) \rightleftharpoons (C_6H_5COOH)_2$$

Initial	1	0
Final	$1 - \alpha$	$\alpha/2$
	$= 1 - 0.8 = 0.2$	$0.8/2 = 0.4$

Total number of moles at equilibrium

$$= 0.2 + 0.4 = 0.6$$

$$i = \frac{\text{Number of moles at equilibrium}}{\text{Number of moles present initially}}$$

$$i = \frac{0.6}{1} = 0.6$$

On substituting all the given values in Eq. (i), we get

$$2 = \frac{0.6 \times 5 \times w \times 1000}{122 \times 30}, \quad w = 2.44 \text{ g}$$

Thus, weight of acid (w) is 2.4 g. Molecules of benzoic acid dimerise in benzene as:

$$2(C_6H_5COOH) \rightleftharpoons (C_6H_5COOH)_2$$

92 For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point? **[JEE Main 2018]**

(a) $[Co(H_2O)_6]Cl_3$
(b) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$
(c) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$
(d) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

Ans. ***(a)***

Key Idea "Addition of solute particles to a pure solvent results to depression in its freezing point."

All the compounds given in question are ionic in nature so, consider their van't Hoff factor (i) to reach at final conclusion.

The solution with maximum freezing point must have minimum number of solute particles. This generalisation can be done with the help of van't Hoff factor (i) i.e.

Number of solute particles $\propto$ van't Hoff factor (i)

Thus, we can say directly

Solution with maximum freezing point will be the one in which soluste with minimum van't Hoff factor is present

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Now, for

$Co(H_2O)_6]Cl_3 \rightleftharpoons [Co(H_2O)_6]^{3+} + 3Cl^-$

van't Hoff factor (i) is 4. Similarly for,

$[Co(H_2O)_5Cl]Cl_2 \cdot H_2O \rightleftharpoons [Co(H_2O)_5Cl]^{2+} + 2Cl^-$ 'i' is 3

$[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O \rightleftharpoons [Co(H_2O)_4Cl_2]^+ + Cl^-$ 'i' is 2

and for $[Co(H_2O)_3Cl_3] \cdot 3H_2O$, 'i' is 1 as it does not show ionisation.

Hence, $[Co(H_2O)_3Cl_3] \cdot 3H_2O$ have minimum number of particles in the solution.

So, freezing point of its solution will be maximum.

93 The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be (K_f for benzene = 5.12 K kg mol^{-1}) **[JEE Main 2017]**

(a) 64.6 % (b) 80.4 %
(c) 74.6 % (d) 94.6 %

Ans. ***(d)***

Let the degree of association of acetic acid (CH_3COOH) in benzene is α, then

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Initial moles	1	0
Moles at equilibrium	$1-\alpha$	$\frac{\alpha}{2}$

$\therefore$ Total moles $= 1-\alpha+\frac{\alpha}{2} = 1-\frac{\alpha}{2}$

or $i = 1-\frac{\alpha}{2}$

Now, depression in freezing point (ΔT_f) is given as

$$\Delta T_f = i K_f m \quad \ldots(i)$$

where, K_f = molal depression constant or cryoscopic constant.

m = molality

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}} = \frac{0.2}{60} \times \frac{1000}{20}$$

Putting the values in Eq. (i)

$$\therefore \quad 0.45 = \left[1-\frac{\alpha}{2}\right](5.12)\left[\frac{0.2}{60} \times \frac{1000}{20}\right]$$

$$1-\frac{\alpha}{2} = \frac{0.45 \times 60 \times 20}{5.12 \times 0.2 \times 1000}$$

$$\Rightarrow \quad 1-\frac{\alpha}{2} = 0.527$$

$$\Rightarrow \quad \frac{\alpha}{2} = 1-0.527$$

$$\therefore \quad \alpha = 0.946$$

Thus, percentage of association = 94.6%

94 Consider the separate solution of 0.500 M C_2H_5OH (aq), 0.100 M $Mg_3(PO_4)_2$ (aq), 0.250 M KBr (aq) and 0.125 M Na_3PO_4 (aq) at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes? **[JEE Main 2014]**

(a) They all have same osmotic pressure
(b) 0.100 M $Mg_3(PO_4)_2$ (aq) has the highest osmotic pressure
(c) 0.125 M Na_3PO_4 (aq) has the highest osmotic pressure
(d) 0.5000 M C_2H_5OH (aq) has the highest osmotic pressure

Ans. ***(a)***

Osmotic pressure, $\pi = i \times MRT$

Where, i = van't Hoff factor, M = Molarity

R = Gas constant,

T = Temperature

For 0.500 M C_2H_5OH (aq), $i = 1$, thus,

$$\pi_{C_2H_5OH}(aq) = 0.5\,RT$$

For 0.100 M $Mg_3(PO_4)_2$ (aq), $i = 5$

$[\because Mg_3(PO_4)_2 \rightleftharpoons Mg^{2+} + 2PO_4^{3-}]$

Thus, $\pi_{Mg_3(PO_4)_2}(aq) = 5 \times 0.1 \times RT = 0.5\,RT$

For 0.250 M KBr (aq), $i = 2$ $[\because KBr \rightleftharpoons K^+ + Br^-]$

Thus, $\pi_{KBr}(aq) = 2 \times 0.250 \times RT = 0.5\,RT$

For 0.125 M Na_3PO_4 (aq), $i = 4$

$[\because Na_3PO_4 \rightleftharpoons 3Na^+ + PO_4^{3-}]$

Thus, $\pi_{Na_3PO_4}(aq) = 4 \times 0.125 \times RT = 0.5\,RT$

Hence, all solutions have same osmotic pressure.

95 The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression **[AIEEE 2011]**

(a) $\alpha = \frac{i-1}{(x+y-1)}$ (b) $\alpha = \frac{i-1}{x+y+1}$

(c) $\alpha = \frac{x+y-1}{i-1}$ (d) $\alpha = \frac{x+y+1}{i-1}$

Ans. ***(a)***

van't Hoff factor (i) is related to degree of dissociation (α) as

$$\alpha = \frac{i-1}{n-1}$$

Here, n are the moles of an electrolyte ($A-B$) dissolved in a solvent.

For A_xB_y, $A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$

Therefore, $\alpha = \frac{i-1}{(x+y-1)}$

96 If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is (K_f = 1.86 K kg mol^{-1}) **[AIEEE 2010]**

(a) 0.0372 K (b) 0.0558 K
(c) 0.0744 K (d) 0.0186 K

Ans. ***(b)***

$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

van't Hoff factor (i) for $Na_2SO_4 = 3$

$$\Delta T_f = i \times K_f \times m = 3 \times 1.86 \times 0.01$$

$$\left[\because m = \frac{0.01\text{ mol}}{1\text{ kg}} = 0.01\text{ mol kg}^{-1}\right]$$

$$= 0.0558\text{ K}$$

97 If α is the degree of dissociation of Na_2SO_4, the van't Hoff factor (i) used for calculating the molecular mass is **[AIEEE 2005]**

(a) $1-2\alpha$ (b) $1+2\alpha$
(c) $1-\alpha$ (d) $1+\alpha$

Ans. ***(b)***

$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$

van't Hoff factor, $i = [1+(y-1)\alpha]$

where y is the number of ions from one mole solute, (in this case = 3), α is the degree of dissociation, $i = (1+2\alpha)$

98 Which one of the following aqueous solutions will exhibit highest boiling point? **[AIEEE 2004]**

(a) 0.01 M Na_2SO_4 (b) 0.01 M KNO_3
(c) 0.015 M urea (d) 0.015 M glucose

Ans. ***(a)***

The colligative property will be given as

$\Delta T_b = i \times k_b \times m$

Where, ΔT_b = Elevation in boiling point

i = van't Hoff factor

K_b = molal elevation constant

m = molality of the solution

From the above equation, it is clear that,

$$\Delta T_b \propto i$$

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This suggests that higher the value of i, larger is the boiling point of the solution.

For 100% dissociation, i = number of ions produced by one mole of solute

Thus, for

(a) Na_2SO_4

$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$

[3 ions]

$\therefore\ i = 3$

(b) KNO_3

$KNO_3 \rightleftharpoons K^+ + NO_3^-$

[2 ions]

$\therefore\ i = 2$

(c) Urea [(NH_2CONH_2) and (d) glucose are poor electrolytes, therefore i for these two solutes are equal to zero.

Hence, 0.01 M Na_2SO_4 possess highest boiling point.

99 Which one of the following statements is false? **[AIEEE 2004]**

(a) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction

(b) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where M is the molarity of the solution

(c) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $BaCl_2 > KCl > CH_3COOH >$ sucrose

(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

Ans. ***(d)***

(a) $p_A = X_A p_A^\circ$ true

(b) $\pi = iMRT = MRT$

true

[If van't Hoff factor, $i = 1$]

(c) $\pi \propto i$

Greater the value of i, larger is the value of π.

i, for $BaCl_2$ (strong electrolyte) is 3.

[$BaCl_2 \rightleftharpoons Ba^{2+} + Cl^-$ (2 ions)]

i for KCl is 2. [$KCl \rightleftharpoons K^+ + Cl^-$]

i for CH_3COOH is

2 [$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$]

But CH_3COOH is weak electrolyte than KCl.

i for sucrose is 1 as it is a non-electrolyte.

Thus,

i (for $BaCl_2$) > KCl > CH_3COOH > sucrose

Thus, (c) is also true.

(d) $\Delta T_f = K_f m$.

K_f is dependent on solvent.

Thus, freezing points = [T (solvent) $- \Delta T_f$] are different.

Thus, (d) is false.

100 In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionisation is 0.3. Taking K_f for water as 1.85, the freezing point of the solution will be nearest to **[AIEEE 2003]**

(a) $-0.480°C$ (b) $-0.360°C$

(c) $-0.260°C$ (d) $+0.480°C$

Ans. ***(a)***

$HX \rightleftharpoons H^+ + X^{-1}$

$\alpha = 0.3$

$i = 1 + \alpha = 1.3$

ΔT_f = molality $\times K_f \times i$

$= 0.2 \times 1.85 \times 1.3 = 0.481°$

$\therefore$ Freezing point $= -0.481°C$

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07

Chemical Equilibrium

TOPIC 1

Chemical Equilibrium, Basic Law of Mass Action and Equilibrium Constant

01 The number of moles of NH_3, that must be added to 2 L of 0.80 M $AgNO_3$ in order to reduce the concentration of Ag^+ ions to 5.0×10^{-8} M ($K_{formation}$ for $[Ag(NH_3)_2]^+ = 1.0\times10^8$) is ..... (Nearest integer)

[Assume no volume change on adding NH_3] **[2021, 27 Aug Shift-I]**

Ans. ***(4)***

Let moles added = a

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

$t=0$	0.8	$\left(\frac{a}{2}\right)$	
$t=\infty$	5×10^{-8}	$\left[\frac{a}{2}-1.6\right]$	0.8

$$\frac{0.8}{5\times10^{-8}\left(\frac{a}{2}-1.6\right)^2}=10^8$$

$$\frac{a}{2}-1.6=0.4 \Rightarrow a=4.$$

02 The equilibrium constant for the reaction

$$A(s)\rightleftharpoons M(s)+\frac{1}{2}O_2(g)$$

is $K_p = 4$. At equilibrium, the partial pressure of O_2 is ..... atm. (Round off to the nearest integer) **[2021, 27 July Shift-II]**

Ans. ***(16)***

According to the equation,

$$A(s) \longrightarrow M(s)+\frac{1}{2}O_2(g)$$

Equilibrium constant, $K_p = p_{O_2}^{1/2} = 4$

where, p = partial pressure

At equilibrium, the partial pressure of O_2 is $p_{O_2} = (4)^2 = 16$ atm.

03 $2SO_2(g)+O_2(g) \longrightarrow 2SO_3(g)$

The above reaction is carried out in a vessel starting with partial pressure $p_{SO_2} = 250$ m bar, $p_{O_2} = 750$ m bar and $p_{SO_3} = 0$. When the reaction is complete, the total pressure in the reaction vessel is ..... m bar. (Round off of the nearest integer). **[2021, 27 July Shift-II]**

Ans. ***(875)***

	$2SO_2(g)$	+ $O_2(g)$	$\longrightarrow$ $2SO_3(g)$
Initial	250 m bar	750 m bar	0
Final	0	$\left(750-\frac{250}{2}\right)$ m bar	250 m bar

$= 625$ m bar

Total final pressure $= 625 + 250$

$= 875$ mbar

04 $PCl_5 \rightleftharpoons PCl_3 + Cl_2, K_c = 1.844$

3.0 moles of PCl_5 is introduced in a 1 L closed reaction vessel at 380 K. The number of moles of PCl_5 at equilibrium is ..... $\times10^{-3}$. (Round off to the nearest integer) **[2021, 27 July Shift-I]**

Ans. ***(1400)***

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

$t=0$	3 moles		
$t=\infty$	$(3-x)$ moles	x	x

$$\frac{[PCl_3][Cl_2]}{[PCl_5]}=\frac{x^2}{3-x}$$

$$= 1.844$$

$$x^2 + 1.844 - 5.532 = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

$$= \frac{-1.844+\sqrt{(1.844)^2+4\times5.532}}{2}$$

$\therefore \quad x = 1.603$

Moles of $PCl_5 = 3 - 1.603$

$= 1.397 \cong 1400\times10^{-3}$

05 The equilibrium constant K_C at 298 K for the reaction $A+B \rightleftharpoons C+D$ is 100. Starting with an equimolar solution with concentrations of A, B, C and D all equal to 1M, the equilibrium concentration of D is ..... $\times10^{-2}$ M. (Nearest integer) **[2021, 26 Aug Shift-II]**

Ans. ***(182)***

	A	+ B	$\rightleftharpoons$ C	+ D
Initially,	1	1	1	1
At equilibrium,	$1-x$	$1-x$	$1+x$	$1+x$

$$\therefore \quad K_C = \left(\frac{1+x}{1-x}\right)^2$$

$$100 = \left(\frac{1+x}{1-x}\right)^2$$

$$\frac{1+x}{1-x} = 10$$

$$x = \frac{9}{11}$$

Moles of $D = 1 + x = 1 + \frac{9}{11} = \frac{20}{11}$

$= 1.818 = 181.8\times10^{-2} = 181.8\times10^{-2}$

$\cong 182\times10^{-2}$ M

06 Value of K_p for the equilibrium reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

at 288 K is 47.9.

The K_C for this reaction at same temperature is ..... (Nearest integer)

($R = 0.083$ L bar $K^{-1}mol^{-1}$) **[2021, 22 July Shift-II]**

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Ans. *(2)*

Given reaction,

$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$

So, Δn_g = [molar of gaseous products-moles of gaseous reactants]

$= 2 - 1 = 1$

$K_p = K_C(RT)^{\Delta n_g}$

where, K_p = equilibrium constant in gaseous state = 47.9

K_C = equilibrium constant

R = gas constant

T = temperature

$\Rightarrow \quad K_C = \dfrac{47.9}{0.083 \times 288}$

$= 2.0038$

$\therefore$ Hence, K_C at same temperature (288 K) is 2.

07 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

In an equilibrium mixture, the partial pressures are $p_{SO_3} = 45$kPa; $p_{O_2} = 530$ Pa and $p_{SO_2} = 45$kPa. The equilibrium constant K_p = ... $\times 10^{-2}$. (Nearest integer)

[2021, 20 July Shift-I]

Ans. *(172)*

On reaction,

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

Given values are :

$p_{SO_3} = 45$kPa, $p_{O_2} = 530$ Pa $= 0.53$ kPa

$p_{SO_2} = 43$ kPa

Now, $K_p = \dfrac{[p_{SO_3(g)}]^2}{[p_{SO_2(g)}]^2 \times [p_{O_2}]}$

On putting given values, we get,

$\Rightarrow \quad K_p = \dfrac{(43)^2}{(45)^2 \times 0.53}$

$= \dfrac{1849}{2025 \times 0.53} = \dfrac{1849}{1073.25}$

$= 1.7228$

$= \dfrac{1.7228 \times 10^2}{10^2}$

$= 172.28 \times 10^{-2} = 172$

Hence, the equilibrium constant, $K_p = 172$.

08 The gas phase reaction

$2A(g) \rightleftharpoons A_2(g)$

at 400 K has $\Delta G^\circ = +25.2$ kJ mol^{-1}. The equilibrium constant K_C for this reaction is ..... $\times 10^{-2}$. (Round off to the nearest integer).

[Use : $R = 8.3$ J mol^{-1} K^{-1}, ln 10 = 2.3]

$\log_{10} 2 = 0.30$, 1 atm = 1 bar]

[antilog $(-0.3) = 0.501$]

[2021, 18 March Shift-II]

Ans. *(1.66)*

$2A(g) \rightleftharpoons A_2(g)$

Given, $\Delta G = 25.2$ kJ mol^{-1}

$= 25200$ J mol^{-1}

$T = 400$ K

According to standard free Gibb's equation,

$\Delta G^\circ = -RT \ln K_p$

$25200 = -2.3 \times 8.3 \times 400 \log(K_p)$

$\log K_p = \dfrac{-25200}{2.3 \times 8.3 \times 400} = -3.3$

$K_p = 10^{-3.3} = 10^{-3} \times 0.501$

$K_p = 5.01 \times 10^{-4}$ bar^{-1}

$K_p = 5.01 \times 10^{-5}$ Pa^{-1}

We know that,

$K_p = K_c(RT)^{\Delta n_g}$

$K_p = K_c(RT)^{-1}$ $[\because \Delta n_g = 1 - 2 = -1]$

$K_p = \dfrac{K_C}{8.3 \times 400}$

$K_c = 5.01 \times 10^{-5} \times 8.3 \times 400$

$\Rightarrow \quad K_c = 166 \times 10^{-5}$ m^3/mol

$= 1.66 \times 10^{-2}$ L/mol

09 Consider the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. The temperature at which $K_C = 20.4$ and $K_p = 600.1$, is ..... K. (Round off to the nearest integer).

[Assume all gases are ideal and $R = 0.0831$ L bar, K^{-1} mol^{-1}].

[2021, 17 March Shift-II]

Ans. *(354)*

The temperature at which $K_C = 20.4$ and $K_p = 600.1$, is 354 K.

Given reaction is,

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Given values are : $K_p = 600.1$

$K_C = 20.4$

Δn_g = number of moles of product − number of moles of reactant

Using relation between K_p and

$K_C = 2 - 1 = 1$

$K_p = K_C(RT)^{\Delta n_g}$

where R is the gas constant = 0.083 L atm/K mol

$\Delta n_g = 1$ (for given reaction)

On putting given values, we will get

$600.1 = 20.4(RT)^1 \Rightarrow T \approx 354$ K

10 For the reaction, $A(g) \rightleftharpoons B(g)$ at 495 K, $\Delta_r G^\circ = -9.478$ kJ mol^{-1}. If we start the reaction in a closed container at 495 K with 22 millimoles of A, the amount of B is the equilibrium mixture is ..... millimoles (Round off to the nearest integer).

[$R = 8.314$ J mol^{-1} K^{-1}, ln 10 = 2.303]

[2021, 16 March Shift-I]

Ans. *(20)*

$A(g) \rightleftharpoons B(g)$

Given, $T = 495$ K, $\Delta_r G^\circ = -9.478$ kJ/mol

We know,

$\Delta G^\circ = -2.303\,RT \log K$

$\because \quad K = \dfrac{[B]}{[A]}$

where, K = equilibrium constant

Now, $\log K = \dfrac{-\Delta G^\circ}{2.303RT}$

$\log K = \dfrac{9.478 \times 1000}{2.303 \times 8.314 \times 495}$

$\therefore \quad \log K = 1$

$\Rightarrow \quad K = 10$

$\Rightarrow \quad \dfrac{[B]}{[A]} = \dfrac{n_B}{n_A} = 10$

Now,

	$A(g)$	$\rightleftharpoons$	$B(g)$
$t = 0$	22		0
$t = t$	$22 - x$		x

$K = \dfrac{[B]}{[A]} = \dfrac{x}{22 - x} = 10$

So, $x = 20$

Milimoles of $B = 20$

11 A homogeneous ideal gaseous reaction, $AB_2(g) \rightleftharpoons A(g) + 2B(g)$ is carried out in a 25 L flask at 27°C. The initial amount of AB_2 was 1 mole and the equilibrium pressure was 1.9 atm. The value of K_p is $x \times 10^{-2}$. The value of x is ..... .

[2021, 26 Feb Shift-I]

Ans. *(73)*

	$AB_2(g)$	$\rightleftharpoons$	$A(g)$	+	$2B(g)$
$t = 0$	1		0		0
$t = t_{eq}$	$(1 - x)$		x		$2x$

$(\Sigma \text{mole})_{t_{eq}} = 1 - x + x + 2x = (1 + 2x)$

Partial pressure (atm)	$\dfrac{1-x}{1+2x}p$	$\dfrac{x}{1+2x}p$	$\dfrac{2x}{1+2x}p$

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[p = Total pressure at equilibrium = 1.9 atm]

Now, at equilibrium $pV = (1+2x)RT$

$\Rightarrow 1+2x = \frac{pV}{RT} = \frac{1.9\times25}{0.082\times300} = 1.93$

[$V = 25$ L, $R = 0.082$ L atm mol^{-1}K^{-1}, $T = 300$ K]

$\Rightarrow x = \frac{1.93-1}{2} = 0.465$

$\Rightarrow K_p = \frac{p_A \times p_B^2}{p_{AB_2}}$

$\Rightarrow \frac{\left(\frac{x}{1+2x}p\right)\times\left(\frac{2x}{1+2x}p\right)^2}{\left(\frac{1-x}{1+2x}p\right)}$

$= \frac{4x^3\times p^3}{(1+2x)^3}\times\frac{(1+2x)}{(1-x)\times p}$

$= \frac{4x^3\times p^2}{(1+2x)^2\times(1-x)}$

$= \frac{4\times(0.465)^3\times(1.9)^2}{(1+2\times0.465)^2\times(1-0.465)}$

$= 0.7285$ atm

$= 72.85\times10^{-2}$ atm

$\simeq 73\times10^{-2} = x\times10^{-2}$

$\therefore x = 73$

12 At 1990 K and 1 atm pressure, there are equal number of Cl_2 molecules and Cl atoms in the reaction mixture. The value of k_p for the reaction $Cl_2(g) \rightleftharpoons 2Cl(g)$ under the above conditions is $x\times10^{-1}$.

The value of x is ..... .

(Rounded off to the nearest integer) **[2021, 24 Feb Shift-I]**

Ans. ***(5)***

$Cl_2(g) \rightleftharpoons 2Cl(g)$

Let, moles of both of Cl_2 and Cl molecule be x.

Partial pressure of Cl is, $p_{Cl} = \frac{x}{2x}\times1 = \frac{1}{2}$

Partial pressure of Cl_2 is

$p_{Cl_2} = \frac{x}{2x}\times1 = \frac{1}{2}$

Now, $K_p = \frac{(p_{Cl})^2}{p_{Cl_2}}$

$\Rightarrow K_p = \frac{(1/2)^2}{1/2} = \frac{1}{2} = 0.5$

or 5×10^{-1}

Hence, $x\times10^{-1}$

$x = 5$

13 For the reaction, $A(g) \longrightarrow B(g)$, the value of the equilibrium constant at 300 K and 1 atm is equal to 100.0. The value of $\Delta_r G$ for the reaction at 300 K and 1 atm in J mol^{-1} is $-xR$, where x is ..... . (Rounded off to the nearest integer)

($R = 8.31$ J mol^{-1} K^{-1} and $\ln10 = 2.3$) **[2021, 24 Feb Shift-I]**

Ans. ***(1380)***

For a reaction, $A(g) \longrightarrow B(g)$

Given, K_p (equilibrium constant) = 100

Temperature = 300 K

Pressure = 1 atm

Formula used

$\Delta G^\circ = -RT\ln K_p$ ...(i)

Here, ΔG° = standard Gibb's free energy

R = gas constant

= 8.31 J mol^{-1} K^{-1}

Put value in Eq (i), we get

$\Delta G^\circ = -R(300)\ln100$

$\Delta G^\circ = -R(300)(2)\ln(10)$

$\because \ln(10) = 2.3$

$\Delta G^\circ = -R(300)(2)(2.3)$

$\Delta G^\circ = -1380R$

Hence, $\Delta G^\circ = -xR$

$x = 1380$

14 An open beaker of water in equilibrium with water vapour is in a sealed container. When few grams of glucose are added to the beaker of water, the rate at which water molecules **[2020, 2 Sep Shift-I]**

(a) leaves the solution decreases

(b) leaves the solution increases

(c) leaves the vapour increases

(d) leaves the vapour decreases

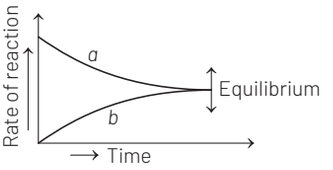
Ans. ***(c)***

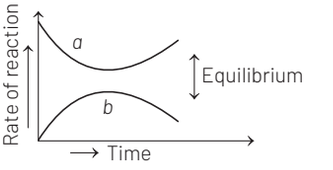
Pure water is a volatile liquid (solvent) whereas glucose is a non-volatile solute.

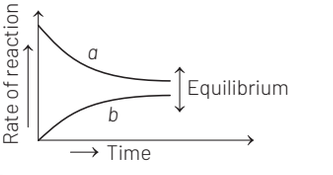
At a certain temperature, water maintains an equilibrium state with water vapour in a sealed container. When glucose is added into water a completely miscible solution is formed in which glucose molecules occupy the inter-molecular space of solvent (H_2O) molecules.

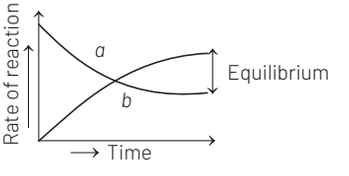
In this solution, fraction of the surface covered by water molecules get reduced. So, the number of solvent molecules escaping from the surface of water as water vapour also reduced.

15 For the equilibrium $A \rightleftharpoons B$, the variation of the rate of the forward (a) and reverse (b) reaction with time is given by **[2020, 4 Sep Shift-I]**

(a)


(b)


(c)


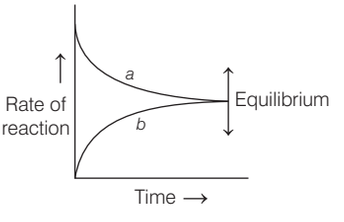
(d)


Ans. ***(a)***

For the equilibrium, $A \rightleftharpoons B$

At equilibrium, $r_a = r_b$

Equilibrium is the condition when a forward chemical reaction and its reverse reaction proceed at equal rates. It can be illustrated by following graph.



16 If the equilibrium constant for $A \rightleftharpoons B + C$ is $K_{eq}^{(1)}$ and that of $B + C = P$ is $K_{eq}^{(2)}$, the equilibrium constant for $A \rightleftharpoons P$ is **[2020, 4 Sep Shift-II]**

(a) $K_{eq}^{(1)}/K_{eq}^{(2)}$ (b) $K_{eq}^{(1)} + K_{eq}^{(2)}$

(c) $K_{eq}^{(1)}K_{eq}^{(2)}$ (d) $K_{eq}^{(2)} - K_{eq}^{(1)}$

Ans. ***(c)***

$A \rightleftharpoons B + C;\ K_{eq}^{(1)} = \frac{[B][C]}{[A]}$ ...(i)

$B + C \rightleftharpoons P;\ K_{eq}^{(2)} = \frac{[P]}{[B][C]}$ ...(ii)

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Equilibrium constant for $A \rightarrow P$

$$A \rightleftharpoons P; K_{eq} = \frac{[P]}{[A]}$$

Multiplying equation (i) and (ii)

$$K_{(eq)}^{(1)} \times K_{(eq)}^{(2)} = \frac{[P]}{[A]} = K_{eq}$$

17 For a reaction, $X + Y = 2Z$

1.0 mol of X, 1.5 mol of Y, and 0.5 mol of Z, were taken in a 1 L vessel and allowed to react. At equilibrium, the concentration of Z was 1.0 mol L^{-1}. The equilibrium constant of the reaction is ..... $\frac{x}{15}$. The value of x is ..... .

[2020, 5 Sep Shift-II]

Ans. ***(16)***

$$\underset{t = t_{eq.}}{x} + \underset{1-a}{y} \rightleftharpoons \underset{1.5-a}{2z} \qquad \underset{0.5+2\alpha\ (a=1\ mol)}{}$$

$$x + y \longrightarrow 2z \quad (a = 0.25)$$

0.75 mol 1.25 mol 1 mol

$$K_{eq} = \frac{[z]^2}{[x][y]} = \frac{1}{0.75 \times 1.25} = \frac{x}{15}$$

$$\Rightarrow \qquad x = \frac{15}{0.75 \times 1.25} = 16$$

18 For the reaction,

$$Fe_2N(s) + \frac{3}{2}H_2(g) \rightleftharpoons Fe(s) + NH_3(g)$$

[2020, 6 Sep Shift-I]

(a) $K_C = K_p(RT)$ (b) $K_C = K_p(RT)^{-1/2}$
(c) $K_C = K_p(RT)^{1/2}$ (d) $K_C = K_p(RT)^{3/2}$

Ans. ***(c)***

$$K_p = K_C(RT)^{\Delta n_g}$$

Δn_g = number of gaseous product molecules – number of gaseous reactant molecules

$$= 1 - \frac{3}{2} = -\frac{1}{2}$$

Now, $\qquad K_p = K_C(RT)^{-1/2}$

$$\therefore \qquad K_C = \frac{K_p}{(RT)^{-1/2}} \Rightarrow K_p(RT)^{1/2}$$

Hence, the correct option is (c).

19 The variation of equilibrium constant with temperature is given below:

Temperature	Equilibrium constant
$T_1 = 25°C$	$K_1 = 10$
$T_2 = 100°C$	$K_2 = 100$

The values of $\Delta H°$, $\Delta G°$ at T_1 and $\Delta G°$ at T_2 (in kJ mol^{-1}) respectively, are close to [use $R = 8.314\ JK^{-1}\ mol^{-1}$]

[2020, 6 Sep Shift-I]

(a) 28.4, –7.14 and –5.71
(b) 0.64, –7.14 and –5.71
(c) 28.4, –5.71 and –14.29
(d) 0.64, –5.71 and –14.29

Ans. ***(c)***

$T_1 = 298\ K, T_2 = 373\ K, K_1 = 10, K_2 = 100$

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H°}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\therefore \log\left(\frac{100}{10}\right) = \frac{\Delta H°}{2.303 \times 8.314}\left(\frac{1}{298} - \frac{1}{373}\right)$$

$$\therefore \qquad \Delta H° = 28.4\ kJ/mol$$

We know that, $\Delta G° = -RT \ln K$

$\therefore \Delta G°$ at

$T_1 = -8.314 \times 298 \times 2.303 \times \log(10)$

$\Rightarrow -5.71\ kJ/mol$

$\Delta G°$ at $T_2 = -8.314 \times 373 \times 2.303 \times \log(100)$

$= -14.29\ kJ/mol$

Hence, the correct option is (c).

20 The value of K_C is 64 at 800 K for the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The value of K_C for the following reaction is

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

[2020, 6 Sep Shift-II]

(a) 1/64 (b) 8 (c) 1/4 (d) 1/8

Ans. ***(d)***

Equilibrium constant for equation,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = 64$$

and for

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g), K_C' = \frac{1}{K_C}$$

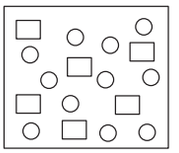
and for equation,

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

$$K_C' = \frac{1}{K_C^{1/2}} = \frac{1}{K_C^{1/2}} = \frac{1}{(64)^{1/2}} = \frac{1}{8}$$

21 In the figure shown below, reactant A (represented by square) is in equilibrium with product B (represented by circle). The equilibrium constant is

[2020, 9 Jan Shift-II]



(a) 4 (b) 2
(c) 8 (d) 1

Ans. ***(b)***

Assuming the reaction to be $A \rightleftharpoons B$,

Equilibrium constant, $K = \frac{[B]}{[A]}$

Number of circles in the figure = 11

Number of squares in the figure = 6

$$\therefore \qquad K = \frac{11}{6} = 1.8 \approx 2$$

22 For the following reactions, equilibrium constants are given :

$$S(s) + O_2(g) \rightleftharpoons SO_2(g);\ K_1 = 10^{52}$$

$$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g);\ K_2 = 10^{129}$$

The equilibrium constant for the reaction,

$$2SO(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ is}$$

[2019, 8 April Shift-II]

(a) 10^{25} (b) 10^{77}
(c) 10^{154} (d) 10^{181}

Ans. ***(a)***

$$S + O_2 \rightleftharpoons SO_2, \quad K_1$$

$$\therefore \qquad SO_2 \rightleftharpoons S + O_2$$

$$K_1' = \frac{1}{K_1}$$

or, $\qquad 2SO_2 \rightleftharpoons 2S + 2O_2$,

$$K_1'' = (K_1')^2 = \frac{1}{K_1^2} \qquad \ldots(i)$$

$$\Rightarrow \qquad 2S + 3O_2 \rightleftharpoons 2SO_3, K_2 \qquad \ldots(ii)$$

Now, [(i) + (ii)] gives

$$2SO_2 + O_2 \rightleftharpoons 2SO_3, K_3$$

The value of equilibrium constant,

$$K_3 = K_2 \times K_1'' = K_2 \times \frac{1}{K_1^2}$$

$$= 10^{129} \times \frac{1}{(10^{52})^2} = 10^{129-104}$$

$$= 10^{25}$$

23 In which one of the following equilibria, $K_p \neq K_c$?

[2019, 12 April Shift-II]

(a) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$
(b) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(c) $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$
(d) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

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Ans. ***(a)***

Key Idea The relationship between K_p and K_c is $K_p = K_c(RT)^{\Delta n_g}$

where, $\Delta n_g = n_{products} - n_{reactants}$

If $\Delta n_g = 0$ then $K_p = K_c$

If $\Delta n_g = +$ ve then $K_p > K_c$

If $\Delta n_g = -$ ve then $K_p < K_c$

Consider the following equilibria reactions

(a) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

$\Delta n_g = n_{product} - n_{reactant} = 2 - (1) = 1$

$\Delta n_g \neq 0 \Rightarrow$ So, $K_p \neq K_c$

(b) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

$\Delta n_g = n_{product} - n_{reactant} = 2 - 2 = 0$

$\Delta n_g = 0 \Rightarrow$ So, $K_p = K_c$

(c) $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$

$\Delta n_g = n_{product} - n_{reactant} = 2 - 2 = 0$

$\Delta n_g = 0 \Rightarrow$ So, $K_p = K_c$

(d) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

$\Delta n_g = n_{product} - n_{reactant} = 2 - 2 = 0$

$\Delta n_g = 0 \Rightarrow$ So, $K_p = K_c$

24 Consider the following reversible chemical reactions,

$A_2(g) + B_2(g) \overset{K_1}{\rightleftharpoons} 2AB(g)$ ...(i)

$6AB(g) \overset{K_2}{\rightleftharpoons} 3A_2(g) + 3B_2(g)$ ...(ii)

The relation between K_1 and K_2 is

(a) $K_2 = K_1^3$ (b) $K_1K_2 = 3$

(c) $K_2 = K_1^{-3}$ (d) $K_1K_2 = \frac{1}{3}$

[2019, 9 Jan Shift-II]

Ans. ***(c)***

(i) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

$K_1 = \frac{[AB]^2}{[A_2][B_2]}$

(ii) $6AB(g) \rightleftharpoons 3A_2(g) + 3B_2(g)$;

$K_2 = \frac{[A_2]^3[B_2]^3}{[AB]^6} = \frac{1}{\left(\frac{[AB]^2}{[A_2][B_2]}\right)^3} = \frac{1}{K_1^3}$,

$\Rightarrow \quad K_2 = K_1^{-3}$

25 The values of $\frac{K_p}{K_C}$ for the following reactions at 300 K are, respectively (At 300 K, $T = 24.62\ dm^3\ atm\ mol^{-1}$)

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

[2019, 10 Jan Shift-I]

(a) 1, 24.62 $dm^3\ atm\ mol^{-1}$, 606.0 $dm^6\ atm^2\ mol^{-2}$

(b) 1, 24.62 $dm^3\ atm\ mol^{-1}$, $1.65 \times 10^{-3}\ dm^{-6}\ atm^{-2}\ mol^2$

(c) 24.62 $dm^3\ atm\ mol^{-1}$, 606.0 $dm^6\ atm^{-2}\ mol^2$, $1.65 \times 10^{-3}\ dm^{-6}\ atm^{-2}\ mol^2$

(d) 1, $4.1 \times 10^{-2}\ dm^{-3} atm^{-1}\ mol$, 606 $dm^6\ atm^2\ mol^{-2}$

Ans. ***(b)***

We know that, the relationship between K_p and K_C of a chemical equilibrium state (reaction) is

$K_p = K_C(RT)^{\Delta n_g}$

$\Rightarrow \quad \frac{K_p}{K_C} = (RT)^{\Delta n_g}$

where, $\Delta n_g = \Sigma n_{Products} - \Sigma n_{Reactants}$

(i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$\Rightarrow \quad (RT)^{2-(1+1)} = (RT)^0 = 1$

(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$\Rightarrow \quad (RT)^{2-1} = RT = 24.62\ dm^3\ atm\ mol^{-1}$

(iii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$\Rightarrow (RT)^{2-(3+1)} = (RT)^{-2}$

$= \frac{1}{(24.62\ dm^3\ atm\ mol^{-1})^2}$

$= 1.649 \times 10^{-3}\ dm^{-6}\ atm^{-2}\ mol^2$

26 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327°C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is ($R = 0.082\ atm\ mol^{-1}K^{-1}$, molar mass of S = 32 g mol^{-1}, molar mass of N = 14 g mol^{-1}) **[2019, 10 Jan Shift-I]**

(a) $0.242 \times 10^{-4}\ atm^2$

(b) $0.242\ atm^2$

(c) $4.9 \times 10^{-3}\ atm^2$

(d) $1 \times 10^{-4}\ atm^2$

Ans. ***(b)***

Molar mass of $NH_4SH = 18 + 33 = 51\ g\ mol^{-1}$

Number of moles of NH_4SH introduced in the vessel

$= \frac{\text{Weight}}{\text{Molar mass}} = \frac{5 \cdot 1}{51} = 0.1\ mol$

	$NH_4SH(s) \rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
Number of moles at $t = 0$	0.1	0		0
At $t = t_{eq}$	0.1(1−0.03)	30% of 0.1 = 0.03		30% of 0.1 = 0.03
Active mass (mol L^{-1})		$\frac{0.03}{3} = 0.01$		$\frac{0.03}{3} = 0.01$

$K_C = \frac{[NH_3][H_2S]}{[NH_4HS(s)]} = \frac{0.01 \times 0.01}{1}$

$= 10^{-4}\ (mol\ L^{-1})^2$

$\Rightarrow K_p = K_C(RT)^{\Delta n_g}$

[where, $\Delta n_g = \Sigma n_{product} - \Sigma n_{reactant}$]

$= 2 - 0 = 2$

$\therefore \quad K_p = K_C(RT)^2$

$= 10^{-4} \times [0.082 \times (273 + 327)]^2\ atm^2$

$= 0.242\ atm^2$

27 Consider the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The equilibrium constant of the above reaction is K_p. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $p_{NH_3} << p_{total}$ at equilibrium) **[2019, 11 Jan Shift-I]**

(a) $\frac{3^{3/2}K_p^{1/2}p^2}{4}$ (b) $\frac{3^{3/2}K_p^{1/2}p^2}{16}$

(c) $\frac{K_p^{1/2}p^2}{16}$ (d) $\frac{K_p^{1/2}p^2}{4}$

Ans. ***(b)***

	$N_2(g) +$	$3H_2(g) \rightleftharpoons$	$2NH_3(g)$
At eq.	$p_{N_2} = P,$	$p_{H_2} = 3P,$	$p_{NH_3} = 2P$

$\Rightarrow$

$p_{(total)} = p_{N_2} + p_{H_2} + p_{NH_3} \simeq p_{N_2} + p_{H_2}$ [$\because p_{(total)} >> p_{NH_3}$]

$= p + 3p = 4p$

Now, $K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = \frac{p^2_{NH_3}}{p \times (3p)^3}$

$= \frac{p^2_{NH_3}}{27 \times p^4} = \frac{p^2_{NH_3}}{27 \times \left(\frac{P}{4}\right)^4}$ [$\because P = 4p$]

$K_p = \frac{p^2_{NH_3} \times 4^4}{3^2 \times 3 \times P^4}$

$\Rightarrow \quad p^2_{NH_3} = \frac{3^2 \times 3 \times P^4 \times K_p}{4^4}$

$\Rightarrow \quad p_{NH_3} = \frac{3 \times 3^{1/2} \times P^2 \times K_p^{1/2}}{4^2}$

$= \frac{3^{3/2} \times P^2 \times K_p^{1/2}}{16}$

28 For the equilibrium, $2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of $\Delta G°$ at 298 K is approximately

(a) −80 kJ mol^{-1} **[2019, 11 Jan Shift-II]**

(b) 100 kJ mol^{-1}

(c) 80 kJ mol^{-1}

(d) −100 kJ mol^{-1}

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Ans. ***(c)***

We know that, $\Delta G^\circ = -2.303 RT \log K$

Also, given equilibrium is

$$2H_2O \rightleftharpoons H_3O^+ + \bar{O}H$$

$$[H^+][OH^-] = 10^{-14} \quad \text{or} \quad K = 10^{-14}$$

$$\therefore \Delta G^\circ = -2.303 \times 8.314\ JK^{-1}\ mol^{-1} \times 298K \times \log 10^{-14}$$

$$= 79881.8\ J\ mol^{-1}$$

$$= 79.8\ kJ \approx 80\ kJ\ mol^{-1}$$

29 Two solids dissociate as follows:

$A(s) \rightleftharpoons B(g) + C(g); K_{p_1} = x\ atm^2$

$D(s) \rightleftharpoons C(g) + E(g); K_{p_2} = y\ atm^2$

The total pressure when both the solids dissociate simultaneously is **[2019, 12 Jan Shift-I]**

(a) $\sqrt{x+y}$ atm (b) $x^2 + y^2$ atm

(c) $(x+y)$ atm (d) $2(\sqrt{x+y})$ atm

Ans. ***(d)***

The equilibrium reaction for the dissociation of two solids is given as:

$$A(s) \rightleftharpoons \underset{p_1}{B(g)} + \underset{p_1+p_2}{C(g)}$$

At equilibrium

$$K_{p_1} = x = p_B \cdot p_C = p_1(p_1 + p_2) \quad ...(i)$$

Similarly,

$$D(s) \rightleftharpoons C(g) + E(g)$$

At equilibrium $p_1 + p_2 \cdot p_2$

$$K_{p_2} = y = p_C \cdot p_E = (p_1 + p_2)p_2 \quad ...(ii)$$

On adding Eq. (i) and (ii), we get.

$$K_{p_1} + K_{p_2} = x + y = p_1(p_1 + p_2) + p_2(p_1 + p_2)$$

$$= (p_1 + p_2)^2$$

or $$\sqrt{x+y} = p_1 + p_2 \quad ...(iii)$$

Now, total pressure is given as

$$p_T = p_B + p_C + p_E$$

$$= p_1 + (p_1 + p_2) + p_2$$

$$= 2(p_1 + p_2) \quad ...(iv)$$

On substituting the value of $p_1 + p_2$ from Eq. (iii) to Eq. (iv), we get

$$p_T = 2\sqrt{x+y}$$

30 In a chemical reaction, $A + 2B \overset{K}{\rightleftharpoons} 2C + D$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is **[2019, 12 Jan Shift-I]**

(a) $\frac{1}{4}$ (b) 16

(c) 1 (d) 4

Ans. ***(d)***

For the given chemical reaction,

	A	+	$2B$	$\rightleftharpoons$	$2C$	+	D
At, $t=0$	a_0		$1.5a_0$		0		0
$t=t_{eq}$	$a_0 - x$		$1.5a_0 - 2x$		$2x$		x

[x = degree of dissociation]

Given, at equilibrium.

$$[A] = [B]$$

$$a_0 - x = 1.5a_0 - 2x$$

$$x = 0.5a_0$$

$$\therefore [A] = a_0 - x = a_0 - 0.5a_0 = 0.5a_0$$

$$[B] = 1.5a_0 - 2x = 1.5a_0 - 2 \times 0.5a_0 = 0.5a_0$$

$$[C] = 2x = 2 \times 0.5a_0 = a_0$$

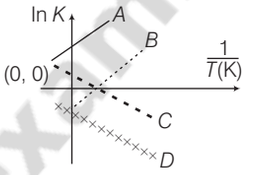
$$[D] = x = 0.5a_0$$

Now, $$K = \frac{[C]^2[D]}{[A][B]^2}$$

Now, substituting the values in above equation, we get

$$K = \frac{(a_0)^2 \times (0.5a_0)}{(0.5a_0) \times (0.5a_0)} = 4$$

31 Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction? **[JEE Main 2018]**



(a) A and B (b) B and C

(c) C and D (d) A and D

Ans. ***(a)***

From thermodynamics,

$$\ln k = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad ...(i)$$

Mathematically, the equation of straight line is

$$y = c + mx \quad ...(ii)$$

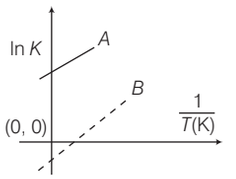
After comparing Eq. (ii) with (i) we get,

$$\text{slope} = \frac{-\Delta H^\circ}{R} \text{ and intercept} = \frac{\Delta S^\circ}{R}$$

Now, we know for exothermic reaction ΔH is negative (–)ve. But here,

$$\text{Slope} = \frac{-\Delta H^\circ}{R} \text{ is positive}$$

So, lines A and B in the graph represent temperature dependence of equilibrium constant K for an exothermic reaction as shown below



32 The equilibrium constant at 298 K for a reaction, $A + B \rightleftharpoons C + D$ is 100. If the initial concentrations of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be **[JEE Main 2016]**

(a) 0.818 (b) 1.818

(c) 1.182 (d) 0.182

Ans. ***(b)***

	A	+	B	$\rightleftharpoons$	C	+	D
Initially at $t=0$	1		1		1		1
At equilibrium	$1-x$		$1-x$		$1+x$		$1+x$

$$K_{eq} = \frac{[C][D]}{[A][B]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = \frac{(1+x)^2}{(1-x)^2}$$

or $$100 = \left(\frac{1+x}{1-x}\right)^2 \quad \text{or} \quad 10 = \frac{1+x}{1-x}$$

or $10 - 10x = 1 + x$

$\Rightarrow$ $10 - 1 = x + 10x$

$$9 = 11x \Rightarrow x = \frac{9}{11} = 0.818$$

$\therefore$ $[D] = 1 + x = 1 + 0.818 = 1.818$

33 The standard Gibbs energy change at 300K for the reaction, $2A \rightleftharpoons B + C$ is 2494. 2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}, [B] = 2$ and $[C] = \frac{1}{2}$. The reaction proceeds in the[R =8.314 JK / mol, e=2.718] **[JEE Main 2015]**

(a) forward direction because $Q < K_c$

(b) reverse direction because $Q < K_c$

(c) forward direction because $Q < K_c$

(d) reverse direction because $Q < K_c$

Ans. ***(b)***

Given, $\Delta G^\circ = 2494.2 J$

$$Q = \frac{[B][C]}{[A]^2} = \frac{2 \times (1/2)}{\left(\frac{1}{2}\right)^2} = 4$$

$\therefore$ We know,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$= 2494.2 + 8.314 \times 300 \ln 4$$

$$= 28747.27 J$$

= positive value

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Also, we have

$$\Delta G = RT \ln \frac{Q}{K}$$

if ΔG is positive, $Q > K$.

Therefore, reaction shifts in reverse direction.

34 For the reaction,

$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$,

if $K_P = K_C (RT)^x$ where the symbols have usual meanings then, the value of x is (assuming ideality). **[JEE Main 2014]**

(a) -1 (b) $-\frac{1}{2}$ (c) $\frac{1}{2}$ (d) 1

Ans. ***(b)***

By using this formula, Equilibrium constant,

$$K_P = K_c (RT)^{\Delta n_g}$$

where Δn_g = (no. of moles of products) − (no. of moles of reactants)

For the given reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$\Delta n_g = 1 - \left[\frac{1}{2} + 1\right] = 1 - \left[\frac{3}{2}\right] = -\frac{1}{2}$$

35 The equilibrium constant (K_c) for the reaction $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction $NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is **[AIEEE 2012]**

(a) 0.02 (b) 2.5×10^2
(c) 4×10^{-4} (d) 50.0

Ans. ***(d)***

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 4 \times 10^{-4}$$

For the reverse reaction,

$$2NO(g) \longrightarrow N_2(g) + O_2(g)$$

$$K_c' = \frac{1}{K_c} = \frac{[N_2][O_2]}{[NO]^2} = \frac{1}{4 \times 10^{-4}} = \frac{10^4}{4}$$

On dividing the reverse reaction by 2

$$NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

$$K_c'' = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]} = \sqrt{K_c'}$$

$$= \sqrt{\frac{10^4}{4}} = \frac{100}{2} = 50$$

36 A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_p is **[AIEEE 2011]**

(a) 1.8 atm (b) 3 atm
(c) 0.3 atm (d) 0.18 atm

Ans. ***(a)***

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Initial	0.5 atm	–
At equilibrium	$(0.5 - p)$	$2p$ atm

This is a case of heterogeneous equilibrium.

C(s) being solid is not considered.

Total pressure of CO_2 and CO gases.

$$p_{CO_2} + p_{CO} = p_{total}$$

$$0.5 - (p + 2p) = 0.8, \; p = 0.3 \text{ atm}$$

$$\therefore \quad p_{CO_2} = 0.5 - 0.3 = 0.2 \text{ atm}$$

$$p_{CO} = 2p = 0.6 \text{ atm}$$

$$K_p = \frac{p_{CO}^2}{p_{CO_2}} = \frac{0.6 \times 0.6}{0.2} = 1.8 \text{ atm}$$

37 In aqueous solution, the ionisation constants for carbonic acid are $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid. **[AIEEE 2010]**

(a) The concentration of CO_3^{2-} is 0.034 M
(b) The concentration of CO_3^{2-} is greater than that of HCO_3^-
(c) The concentration of H^+ and HCO_3^- are approximately equal
(d) The concentration of H^+ is double that of CO_3^{2-}

Ans. ***(c)***

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-; \; K_1 = 4.2 \times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}; \quad K_2 = 4.8 \times 10^{-11}$$

$$K_1 >> K_2$$

$$\therefore \; [H^+] = [HCO_3^-] \Rightarrow K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

So, $[CO_3^{2-}] = K_2 = 4.8 \times 10^{-11}$

38 For the following three reactions I, II and III, equilibrium constants are given **[AIEEE 2008]**

I. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); \; K_1$

II. $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_1$

III. $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); \; K_3$

Which of the following relations is correct?

(a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$
(c) $K_3 = K_1K_2$ (d) $K_3K_2^3 = K_1^2$

Ans. ***(c)***

As equation 'III' is obtained on adding equation 'I' and equation 'II', so $K_3 = K_1 \cdot K_2$.

39 The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal, then the ratio of total pressure at these equilibria is **[AIEEE 2008]**

(a) 1 : 36 (b) 1 : 1
(c) 1 : 3 (d) 1 : 9

Ans. ***(a)***

Let the total pressure at equilibrium for the given two reactions are p_1 and p_2, respectively.

For first reaction,

$$X \rightleftharpoons 2Y$$

Initial	1 mol	0
At equilibrium	$(1-\alpha)$	2α

Total moles = $(1 - \alpha) + 2\alpha$

[Here, α is the degree of dissociation]

$$= (1 + \alpha)$$

$$p_X = \frac{1-\alpha}{1+\alpha} p_1$$

[$\because$ Partial pressure = (Total no. of moles) × (Total pressure)]

$$p_Y = \frac{2\alpha}{1+\alpha} p_1$$

$$K_{p_1} = \frac{\left(\frac{2\alpha}{1+\alpha} p_1\right)^2}{\left(\frac{1-\alpha}{1+\alpha} p_1\right)} = \frac{4\alpha^2}{1-\alpha^2} P_1 = 4\alpha^2 P_1$$

[$\because \alpha^2 <<< 1$]

For second reaction

$$Z \rightleftharpoons P + Q$$

Initial	1 mol	0	0
At equilibrium	$1-\alpha$	α	α

Total moles = $1 - \alpha + \alpha + \alpha = (1 + \alpha)$

$$p_Z = \frac{1-\alpha}{1-\alpha} P_2$$

$$p_P = \frac{\alpha}{1+\alpha} P_2$$

and

$$p_Q = \frac{\alpha}{1+\alpha} P_2$$

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$$K_{P_2} = \frac{\left(\frac{\alpha}{1+\alpha}P_2\right)\left(\frac{\alpha}{1+\alpha}P_2\right)}{\left(\frac{1+\alpha}{1+\alpha}P_2\right)}$$

$$= \frac{\alpha^2 P_2}{1-\alpha^2} = \alpha^2 P_2 \qquad [\because \alpha^2 <<< 1]$$

$$\frac{K_{P_1}}{K_{P_2}} = \frac{4\alpha^2 P_1}{\alpha^2 P_2}$$

$$\Rightarrow \qquad \frac{1}{9} = \frac{4P_1}{P_2} \Rightarrow \frac{P_1}{P_2} = \frac{1}{36}$$

40 The equilibrium constant K_c for the reaction

$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

is 4.9×10^{-2}. The value of K_c for the reaction

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

will be **[AIEEE 2006]**

(a) 416 (b) 2.40×10^{-3}
(c) 9.8×10^{-2} (d) 4.9×10^{-2}

Ans. ***(a)***

Equilibrium constant for the reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$K_c = \frac{1}{4.9 \times 10^{-2}}$$

and for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_c = \left(\frac{1}{4.9 \times 10^{-2}}\right)^2 = \frac{10^4}{(4.9)^2}$$

$$= 416.490 \approx 416$$

41 Phosphorus pentachloride dissociates as follows, in a closed reaction vessel,

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

If total pressure, at equilibrium, of the reaction mixture is p and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be **[AIEEE 2006]**

(a) $\left(\frac{x}{x+1}\right)p$ (b) $\left(\frac{2x}{1-x}\right)p$
(c) $\left(\frac{x}{x-1}\right)p$ (d) $\left(\frac{x}{1-x}\right)p$

Ans. ***(a)***

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initially	1		0		0
At equilibrium	$(1-x)$		x		x

Total number of moles at equilibrium

$= (1-x) + x + x = 1 + x$

$$p_{PCl_3} = \left[\frac{x}{1+x}\right]p$$

42 An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm . The equilibrium constant for the decomposition of NH_4HS at this temperature is **[AIEEE 2005]**

(a) 0.11 (b) 0.17
(c) 0.18 (d) 0.30

Ans. ***(a)***

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
Initially	1		0.5		0
At equilibrium	$(1-x)$		$(0.5+x)$		x

Total pressure at equilibrium

$= p_{NH_3} + p_{H_2S}$

$= 0.5 + x + x = 0.84$

$\therefore \quad x = 0.17$ atm

$\therefore \quad p_{NH_3} = 0.50 + 0.17 = 0.67$ atm

$p_{H_2S} = 0.17$ atm

$\therefore \quad K_p = p_{NH_3} \cdot p_{H_2S}$

$= 0.67 \times 0.17 = 0.114$ atm

43 For the reaction,

$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$[K_c = 1.8 \times 10^{-6}$ at 184°C, $R = 0.00831$ kJ/(mol K)]

When K_p and K_c are compared at 184°C it is found that **[AIEEE 2005]**

(a) whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure
(b) $K_p = K_c$
(c) K_p is less than K_c
(d) K_p is greater than K_c

Ans. ***(d)***

$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$K_c = 1.8 \times 10^{-6}$ at 184° C (= 457 K)

$R = 0.00831$ kJ mol^{-1} K^{-1}

$K_p = K_c (RT)^{\Delta n_g}$

where, Δn_g = (gaseous products − gaseous reactants)

$= 3 - 2 = 1$

$\therefore K_p = 1.8 \times 10^{-6} \times 0.00831 \times 457$

$= 6.836 \times 10^{-6} > 1.8 \times 10^{-6}$

Thus, $K_p > K_c$.

44 What is the equilibrium expression for the reaction

$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$? **[AIEEE 2004]**

(a) $K_c = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$ (b) $K_c = \frac{[P_4O_{10}]}{5[P_4][O_2]^5}$

(c) $K_c = [O_2]^5$ (d) $K_c = \frac{1}{[O_2]^5}$

Ans. ***(d)***

In the expression for equilibrium constant (K_p or K_c), species in solid state are not written (*i.e.*, their molar concentrations are taken as 1)

$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

Thus, $K_c = \frac{1}{[O_2]^5}$

45 For the reaction, $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, the K_p / K_c is equal to **[AIEEE 2004]**

(a) $1/RT$ (b) RT (c) $\sqrt{RT}$ (d) 1.0

Ans. ***(a)***

$$K_p = K_c (RT)^{\Delta n_g}$$

Δn_g = (Sum of coefficients of gaseous products) − (Sum of coefficients of gaseous reactants)

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$$

$\therefore \quad \Delta n_g = 1 - 2 = -1$

$\therefore \quad K_p = K_c (RT)^{-1}$

$\therefore \quad \frac{K_p}{K_c} = (RT)^{-1} = \frac{1}{(RT)}$

46 For the reaction equilibrium,

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1}, respectively. The value of K_c for the reaction is **[AIEEE 2003]**

(a) 3.3×10^2 mol L^{-1}
(b) 3×10^{-1} mol L^{-1}
(c) 3×10^{-3} mol L^{-1}
(d) 3×10^3 mol L^{-1}

Ans. ***(c)***

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(1.2 \times 10^{-2})^2}{4.8 \times 10^{-2}}$$

$= 3 \times 10^{-3}$ mol L^{-1}

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47 For the following reaction in gaseous phase

$CO + \frac{1}{2}O_2 \longrightarrow CO_2$. K_c / K_p is

[AIEEE 2002]

(a) $(RT)^{1/2}$ (b) $(RT)^{-1/2}$
(c) (RT) (d) $(RT)^{-1}$

Ans. ***(a)***

According to the relationship of K_p and K_c,

$K_p = K_c (RT)^{\Delta n_g} \Rightarrow \Delta n_g = 1 - 1.5 = -0.5$

$$K_p = K_c (RT)^{-1/2} = \frac{K_c}{(RT)^{1/2}}$$

$$\Rightarrow \frac{K_c}{K_p} = (RT)^{1/2}$$

TOPIC 2
Le-Chatelier's Principle

48 When 5.1 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 20% of the solid decomposes into gaseous ammonia and hydrogen sulphide. The K_{p_2} for the reaction at 27°C is $x \times 10^{-2}$. The value of x is ..... . (Integer answer)

[Given, $R = 0.082$ L atm K^{-1} mol^{-1}]

[2021, 27 Aug Shift-II]

Ans. ***(6)***

51 g of NH_4HS = 1 mol

5.1 g of $NH_4HS = \frac{1}{51} \times 5.1 = 0.1$ mol

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

At $t = 0$, 0.1

At $t = t$, $0.1(1-\alpha)$ 0.1α 0.1α

It is given that dissociation is 20% from 100 moles.

∴20 moles get dissociated.

20% dissociation from 1 mol 20/100 = 0.2 moles get dissociated.

$\alpha = 0.2$

$$\because K_C = \frac{[NH_3][H_2S]}{[NH_4HS]} = \frac{[NH_3][H_2S]}{1}$$

(Concentration of solid is assumed as 1)

$$[NH_3] = \frac{\text{Number of moles of } NH_3(g)}{\text{Volume (in L)}} = \frac{0.1\alpha}{2}$$

$$[H_2S] = \frac{\text{Number of moles of } H_2S}{\text{Volume (in L)}} = \frac{0.1\alpha}{2}$$

$$K_C = \frac{0.1\alpha}{2} \times \frac{0.1\alpha}{2} = \frac{0.1 \times 0.2}{2} \times \frac{0.1 \times 0.2}{2} = 10^{-4}$$

$\therefore K_p = K_C (RT)^{\Delta n}$

[Δn = change in the number of gaseous moles = 2]

$K_p = 10^{-4} \times (0.08 \times 300)^2$

$K_p = 10^{-4} \times (24)^2 = 0.06$

$x \times 10^{-2} = 0.06$

$$\Rightarrow x = \frac{0.06}{10^{-2}} = 0.06 \times 10^2 = 6$$

$x = 6$ is the answer.

49 Consider the following reaction :

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $\Delta H° = +58$ kJ

For each of the following cases (*A*, *B*), the direction in which the equilibrium shifts is

(*A*) temperature is decreased.

(*B*) pressure is increased by adding N_2 at constant *T*.

[2020, 5 Sep Shift-I]

(a) (*A*) towards product, (*B*) towards reactant
(b) (*A*) towards reactant, (*B*) no change
(c) (*A*) towards reactant, (*B*) towards product
(d) (*A*) towards product, (*B*) no change

Ans. ***(b)***

$N_2O_4(s) \rightleftharpoons 2NO_2(s)$; $\Delta H° = +58$ kJ

Because in case of an endothermic reaction (ΔH = + ve), the equilibrium constant increases with rise in temperature and hence, the reaction moves in forward direction. On adding N_2, pressure is increased at constant *T*, and volume would also be constant, so no change is observed.

50 For the reaction,

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$,

$\Delta H = -57.2$ kJ mol^{-1} and $K_c = 1.7 \times 10^{16}$. Which of the following statement is incorrect?

[2019, 10 April Shift-II]

(a) The equilibrium constant decreases as the temperature increases
(b) The addition of inert gas at constant volume will not affect the equilibrium constant
(c) The equilibrium will shift in forward direction as the pressure increases
(d) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required

Ans. ***(d)***

The explanation of given statements are as follows :

(a) For the given equilibrium, ΔH is negative, so the equilibrium constant will decrease with increase in temperature and the equilibrium will shift in the backward direction.
Thus, statement (a) is correct.

(b) When inert gas is added at constant volume and constant temperature, an equilibrium remains undisturbed.
Thus, statement (b) is correct.

(c) For the equilibrium,
$\Delta n_g = 2 - (2 + 1) = -1$, i.e. (–ve)
So, increase in pressure will shift the equilibrium in the forward direction.
Thus, statement (c) is correct.

(d) The reaction takes place in the presence of a catalyst which is $V_2O_5(s)$ in contact process or $NO(g)$ in chamber process.
Thus, statement (d) is incorrect.

51 The exothermic formation of ClF_3 is represented by the equation

$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$; $\Delta H_r = -329$ kJ

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3? **[AIEEE 2005]**

(a) Adding F_2
(b) Increasing the volume of the container
(c) Removing Cl_2
(d) Increasing the temperature

Ans. ***(a)***

Reaction is exothermic. By Le-Chatelier principle, a reaction is spontaneous in forward side (in the direction of formation of more ClF_3). If F_2 is added, temperature is lowered and ClF_3 is removed.

52 One of the following equilibria is not affected by change in volume of the flask **[AIEEE 2002]**

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(c) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

Ans. ***(c)***

Change in volume affects number of moles per unit volume and move in the direction which undo the change.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Number of moles of reactants and products are equal

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08

Ionic Equilibrium

TOPIC 1
Ostwald's Dilution Law

01 The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionisation constant, K_a of the acid is **[AIEEE 2012]**

(a) 3×10^{-1} (b) 1×10^{-3}
(c) 1×10^{-5} (d) 1×10^{-7}

Ans. ***(c)***

$HQ = H^+ + Q^-$

$[H^+] = \sqrt{K_a C}$ by Ostwald's dilution law

$[H^+] = 10^{-pH} = 10^{-3}$ M

$C = 0.1$ M

Thus, $10^{-3} = \sqrt{K_a \times 0.1}$

$10^{-6} = K_a \times 0.1 \Rightarrow K_a = 10^{-5}$

Alternate method

$HQ \rightleftharpoons H^+ + Q^-$

0.1 M 0 0

Initial concentration

Given, pH = 3, this suggests $[H^+] = 10^{-3}$ M at equilibrium.

Thus, $[Q^-]$ at equilibrium $= 10^{-3}$ M

Hence, $[HQ] = 0.1\text{ M} - 10^{-3}\text{ M}$

≈ 0.1 M $[\because 10^{-3}\text{ M} <<< 0.1\text{ M}]$

K_a for the above reaction is given by

$$K_a = \frac{[H^+][Q^-]}{[HQ]} = \frac{[10^{-3}][10^{-3}]}{[0.1]}$$

$\Rightarrow K_a = 1\times10^{-5}$

02 The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10}, respectively. The overall dissociation constant of the acid will be **[AIEEE 2007]**

(a) 5.0×10^{-5} (b) 5.0×10^{15}
(c) 5.0×10^{-15} (d) 0.2×10^{5}

Ans. ***(c)***

The overall dissociation constant of the acid is

$K = K_1 \times K_2$

$= 1.0\times10^{-5}\times5.0\times10^{-10} = 5\times10^{-15}$

TOPIC 2
Acid Base Concepts

03 Assuming that $Ba(OH)_2$ is completely ionised in aqueous solution under the given conditions the concentration of H_3O^+ ions in 0.005 M aqueous solution of $Ba(OH)_2$ at 298 K is ..... $\times10^{-12}$ mol L^{-1}. (Nearest integer) **[2021, 25 July Shift-II]**

Ans. ***(1)***

$Ba(OH)_2$ is completely ionised in aqueous solution.

$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$

$[Ba(OH)_2] = 0.005$M

$\Rightarrow 2\times0.005 \Rightarrow 0.01$

$[OH^-] = 10^{-2}$

At 298 K, in aqueous solution ;

$[H_3O^+][OH^-] = 10^{-14}$

$$[H_3O^+] = \frac{10^{-14}}{10^{-2}} = 10^{-12}$$

$[H_3O^+] = 1\times10^{-12}$ M

04 0.01 moles of a weak acid HA ($K_a = 2.0\times10^{-6}$) is dissolved in 1.0 L of 0.1 M HCl solution. The degree of dissociation of HA s ..... $\times10^{-5}$ (Round off to the nearest integer).

[Neglect volume change on adding HA. Assume degree of dissociation << 1] **[2021, 17 March Shift-I]**

Ans. ***(2)***

Given, $[HA] = 0.01$

$[HCl] = 0.1$ M

When strong acid (HCl) is completely dissociated,

$$\underset{0.1}{HCl} \longrightarrow \underset{0.1}{H^+(aq)} + \underset{0.1}{Cl^-(aq)}$$

For weak acid, dissociation is very less,

$$HA \rightleftharpoons H^+(aq) + A^-(aq)$$

$t = 0$ 0.01 0.1 0

$t = t_{eq}$ $0.01 - 0.01\alpha$ $0.1 + 0.01\alpha$ 0.01α

$$K_a = \frac{[H^+][A^-]}{[HA]} = 2\times10^{-6}$$

$$\Rightarrow \frac{(0.1+0.01\alpha)(0.01\alpha)}{(0.01-0.01\alpha)} = 2\times10^{-6}$$

As $0.01\alpha << 0.1$ $[H^+] = 0.1$

and $0.01\alpha << 0.01$ $[HA] = 0.01$

$$\therefore \quad 2\times10^{-6} = \frac{(0.1)(0.01\alpha)}{0.01}$$

$\Rightarrow \alpha = 2\times10^{-5}$

$\Rightarrow x = 2$

05 The decreasing order of electrical conductivity of the following aqueous solution is

0.1 M formic acid (*A*),

0.1 M acetic acid (*B*),

0.1 M benzoic acid (*C*). **[2019, 12 April Shift-II]**

(a) $A > C > B$ (b) $C > B > A$
(c) $A > B > C$ (d) $C > A > B$

Ans. ***(a)***

Electrical conductivity of the given aqueous solutions depends on the degree of ionisation. Degree of ionisation is directly proportional to the acidic strength. Electron withdrawing groups (EWGs) increases the stability of the carboxylate ion by dispersing the negative charge through resonance

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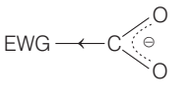
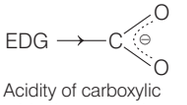
effect on the conjugate while electron donating groups (EDGs) decreases the stability of the carboxylate ion by intensifying the negative charge.



Acidity of carboxylic acids increases due to the presence of electron withdrawing groups (EWGs)



Acidity of carboxylic acids decreases due to the presence of electron donating groups

The correct order of acidic strength and electrical conductivity is as follows:

$\underset{A}{HCOOH} > \underset{C}{PhCOOH} > \underset{B}{CH_3COOH}$

06 Which of the following are Lewis acids? **[JEE Main 2018]**

(a) PH_3 and BCl_3 (b) $AlCl_3$ and $SiCl_4$
(c) PH_3 and $SiCl_4$ (d) BCl_3 and $AlCl_3$

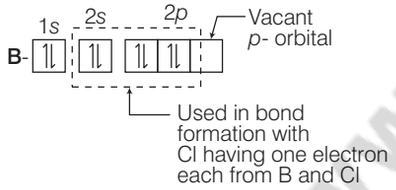
Ans. ***(d)***

Lewis acids are defined as,
"Electron deficient compounds which have the ability to accept atleast one lone pair."

The compound given are

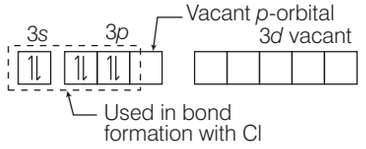
PH_3 Octet complete although P has vacant 3*d*-orbital but does not have the tendency to accept lone pair in it. Hence, it cannot be considered as Lewis acid.

BCl_3 Incomplete octet with following orbital picture.



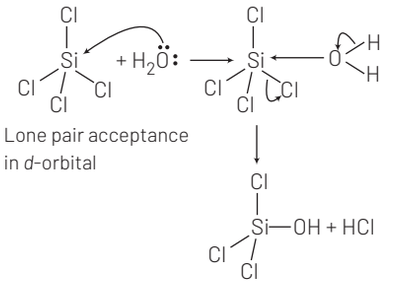
Hence, vacant *p*-orbital of B can accept one lone pair thus it can be considered as Lewis acid.

$AlCl_3$ -Similar condition is visible in $AlCl_3$ as well i.e. Al
(Valence orbital only)=



Hence this compound can also be considered as Lewis acid.

$SiCl_4$ - Although this compound does not have incomplete octet but it shows the tendency to accept lone pair of electrons in its vacant *d*-orbital. This tendency of $SiCl_4$ is visible in following reaction.



Thus option (b) and (d) both appear as correct but most suitable answer is (d) as the condition of a proper Lewis acid is more well defined in BCl_3 and $AlCl_3$.

07 Three reactions involving $H_2PO_4^-$ are given below **[AIEEE 2010]**

I. $H_3PO_4 + H_2O \longrightarrow H_3O^+ + H_2PO_4^-$

II. $H_2PO_4^- + H_2O \longrightarrow HPO_4^{2-} + H_3O^+$

III. $H_2PO_4^- + OH^- \longrightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid?

(a) II only (b) I and II
(c) III only (d) I only

Ans. ***(a)***

Only in reaction (II), $H_2PO_4^-$, gives H^+ to H_2O. Thus, behaves as an acid.

08 Four species are listed below

I. HCO_3^- II. H_3O^+
III. HSO_4^- IV. HSO_3F

Which one of the following is the correct sequence of their acid strength? **[AIEEE 2008]**

(a) IV < II < III < I (b) II < III < I < IV
(c) I < III < II < IV (d) III < I < IV < II

Ans. ***(c)***

Conjugate bases of the given species are

Species	Conjugate base
HCO_3^-	CO_3^{2-}
H_3O^+	H_2O
HSO_4^-	SO_4^{2-}
HSO_3F	HSO_3^-

Since, strong acid has a weak conjugate base. Thus, the basic strength of the conjugate bases of the given acid is opposite to their acidic strength. The basic strength of the conjugate bases of the given acids follows the order

$HSO_3^- < H_2O < SO_4^{2-} < CO_3^{2-}$

Hence, the acidic strength follows the order

$HSO_3F > H_3O^+ > HSO_4^- > HCO_3^-$

09 What is the conjugate base of OH^-? **[AIEEE 2005]**

(a) O^{2-} (b) O^-
(c) H_2O (d) O_2

Ans. ***(a)***

Conjugate base is formed by loss of H^+.

$OH^- \longrightarrow \underset{\text{Conjugate base}}{O^{2-}} + H^+$

O^{2-} is the conjugate base of OH^-.

10 The conjugate base of $H_2PO_4^-$ is **[AIEEE 2004]**

(a) PO_4^{3-} (b) $P_2O_5^{2-}$
(c) H_3PO_4 (d) HPO_4^{2-}

Ans. ***(d)***

H_3PO_4 is a tribasic acid, thus ionises in three steps

I : $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$
II : $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$
III : $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

Conjugate base is formed when an acid loses its proton. Thus, HPO_4^{2-} is the conjugate base of $H_2PO_4^-$ (which is an acid in step II, but is the conjugate base of H_3PO_4 in step I).

11 Which one of the following substances has the highest proton affinity ? **[AIEEE 2003]**

(a) H_2O (b) H_2S
(c) NH_3 (d) PH_3

Ans. ***(c)***

The tendency to accept the proton by the donation of their lone pairs of electron is called proton affinity. This proton affinity is also called basicity. Therefore, the molecule which donates their lone pairs electron more readily, is said to be more basic. Since, N can easily donate their lone pairs of electrons than O, S and P due to their smaller size and low electronegativity.

Thus, NH_3 possess the highest proton affinity. On the other hand, due to higher electronegativity of O, it cannot donate their electron pair easily while *P* possess a larger size, becomes less basic in nature.

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12 Which one of the following species acts as both Bronsted acid and base? **[AIEEE 2002]**

(a) $H_2PO_2^-$ (b) HPO_3^{2-}
(c) HPO_4^{2-} (d) All of these

Ans. ***(c)***

According to Bronsted Lowry concept of acids and bases, an acid is a proton donor whereas a base is a proton acceptor.

Thus, according to this concept, HPO_4^{2-} can easily donate a proton and also accepts a proton on reaction with water.

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$$
$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^{2-} + OH^-$$

TOPIC 3
Solubility Product and Common Ion Effect

13 The molar solubility of $Zn(OH)_2$ in 0.1 M NaOH solution is $x \times 10^{-18}$ M. The value of x is ..... (Nearest integer)

(Given; The solubility product of $Zn(OH)_2$ is 2×10^{-20}).

[2021, 1 Sep Shift-II]

Ans. ***(2)***

$$Zn(OH)_2 \rightleftharpoons \underset{S}{Zn^{2+}} + \underset{2S}{2OH^-}$$

Due to common-ion effect (presence of NaOH) the concentration of OH^- will be $(2S + 0.1) \approx 0.1$ ($\because 0.1 >> 2S$)

$\therefore$ Solubility of product,

$$K_{sp} = (0.1)^2 \times S$$
$$2 \times 10^{-20} = 0.01 \times S$$
$$\Rightarrow \quad S = \frac{2 \times 10^{-20}}{0.01} = 2 \times 10^{-18}$$
$$\therefore \quad x = 2$$

Hence, answer is 2.

14 A_3B_2 is a sparingly soluble salt of molar mass M ($g\ mol^{-1}$) and solubility x g L^{-1}. The solubility product satisfies $K_{sp} = a\left(\frac{x}{M}\right)^5$. The value of a is ..... (Integer answer)

[2021, 31 Aug Shift-I]

Ans. ***(108)***

$$A_3B_2 \rightleftharpoons \underset{3S}{3A^{2+}(aq)} + \underset{2S}{2B^{3-}(aq)}$$
$$K_{sp} = [A^{2+}]^3 [B^{3-}]^2$$
$$K_{sp} = (3S)^3 (2S)^2 = 108\, S^5$$

Also, $S = \frac{x}{m}$

$$K_{sp} = 108\left(\frac{x}{m}\right)^5$$

Given that, $K_{sp} = a\left(\frac{x}{m}\right)^5$

$\therefore \quad a = 108$

15 A solution is 0.1 M in Cl^- and 0.001 M in CrO_4^{2-}. Solid $AgNO_3$ is gradually added to it.

Assuming that the addition does not change in volume and $K_{sp}(AgCl) = 1.7 \times 10^{-10}\ M^2$ and $K_{sp}(Ag_2CrO_4) = 1.9 \times 10^{-12} M^3$

Select correct statement from the following **[2021, 20 July Shift-II]**

(a) AgCl precipitates first because its K_{sp} is high.
(b) Ag_2CrO_4 precipitates first as its K_{sp} is low.
(c) Ag_2CrO_4 precipitates first because the amount of Ag^+ needed is low.
(d) AgCl will precipitate first as the amount of Ag^+ needed to precipitate is low.

Ans. ***(d)***

$K_{sp}(AgCl) = 1.7 \times 10^{-10}\ M^2$

$K_{sp}(Ag_2CrO_4) = 1.9 \times 10^{-12}\ M^3$

(i) $[Ag^+]$ required to ppt. AgCl(s)

$$K_{sp} = [Ag^+][Cl^-]$$
$$\Rightarrow \quad 1.7 \times 10^{-10} = [Ag^+][0.1]$$
$$[Ag^+] = 1.7 \times 10^{-10}$$

(ii) $[Ag^+]$ required to ppt. $Ag_2CrO_4(s)$

K_{sp} = Ionic product $= [Ag^+]^2[CrO_4^{2-}]$

$$\Rightarrow 1.9 \times 10^{-12} = [Ag^+]^2[0.001]$$
$$[Ag^+] = \sqrt{1.9 \times 10^{-9}}$$
$$= \sqrt{19} \times 10^{-5}$$
$$= 4.3 \times 10^{-5}$$

$\therefore [Ag^+]$ required to precipitate AgCl is low, so AgCl will precipitate first.

16 The solubility of $CdSO_4$ in water is 8.0×10^{-4} mol L^{-1}. Its solubility in 0.01 M H_2SO_4 solution is ..... $\times 10^{-6}$ mol L^{-1}. (Round off to the nearest integer)

(Assume that, solubility is much less than 0.01 M)

[2021, 18 March Shift-II]

Ans. ***(64)***

Given, solubility in water

$(S) = 8.0 \times 10^{-4}$ mol L^{-1}

In pure water,

$K_{sp} = S^2 = (8 \times 10^{-4})^2 = 64 \times 10^{-8}$

In 0.01 M H_2SO_4

$$H_2SO_4(aq) \longrightarrow \underset{0.02}{2H^+(aq)} + \underset{0.01}{SO_4^{2-}(aq)}$$
$$\underset{x}{CdSO_4(s)} \rightleftharpoons \underset{x}{Cd^{2+}(aq)} + \underset{(x+0.01)}{SO_4^{2-}(aq)}$$

$K_{sp} = x(x + 0.01) = 64 \times 10^{-8}$

$x + 0.01 \cong 0.01$ M

So, $x(0.01) = 64 \times 10^{-8} \Rightarrow x = 64 \times 10^{-6}$ M

17 The oxygen dissolved in water exerts a partial pressure of 20 kPa in the vapour above water. The molar solubility of oxygen in water is ..... $\times 10^{-5}$ mol dm^{-3}.

(Round off to the nearest integer).

[Given, Henry's law constant (K_H) $= 8.0 \times 10^4$ kPa for O_2, density of water with dissolved oxygen $= 1.0$ kg dm^{-3}]. **[2021, 17 March Shift-I]**

Ans. ***(25)***

Given, partial pressure of $O_2 = 20$ kPa

K_H (Henry's constant) $= 8 \times 10^4$ kPa

From Henry's law,

$$p(g) = [K_H]\chi_{O_2}$$

where, χ_{O_2} = solubility of oxygen

$$20 \times 10^3 = (8 \times 10^4 \times 10^3)\,\chi_{O_2}$$
$$\Rightarrow \quad \chi_{O_2} = \frac{20}{8 \times 10^4}$$

Solubility $= 2.5 \times 10^{-4} = 25 \times 10^{-5}$

18 Two salts A_2X and MX have the same value of solubility product of 4.0×10^{-12}. The ratio of their molar solubilities i.e $\frac{S(A_2X)}{S(MX)} =$ .....

(Round off to the nearest integer)

[2021, 16 March Shift-I]

Ans. ***(50)***

Let the solubility of A_2X be 'S'.

$$A_2X(s) \rightleftharpoons \underset{2S}{2A^+(aq)} + \underset{S}{X^{2-}(aq)};$$
$$K_{sp_1} = 4 \times 10^{-12}$$
$$K_{sp_1} = [A^+]^2[X^{2-}]$$
$$4 \times 10^{-12} = (2S)^2(S)$$
$$4 \times 10^{-12} = 4S^3 \Rightarrow S = 10^{-3}\ M$$

Let the solubility of MY be 'S_1'.

$$MY(s) \rightleftharpoons \underset{S_1}{M^+(aq)} + \underset{S_1}{Y^-(aq)},$$

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$$K_{sp_2} = 4 \times 10^{-12}$$
$$K_{sp_2} = [M^+][Y^-]$$
$$K_{sp_2} = (S_1)^2$$
$$4 \times 10^{-12} = (S_1)^2$$
$$\Rightarrow \quad S_1 = 2 \times 10^{-6} \text{ M}$$
$$\frac{[A_2Y]}{[MY]} = \frac{S}{S_1} = \frac{10^{-4}}{2 \times 10^{-6}} = 50$$

19 The solubility of $Ca(OH)_2$ in water is [Given: The solubility product of $Ca(OH)_2$ in water = 5.5×10^{-6}]

[2021, 25 Feb Shift-II]

(a) 1.11×10^{-2} (b) 1.11×10^{-6}
(c) 1.77×10^{-2} (d) 1.77×10^{-6}

Ans. ***(a)***

Let, solubility of $Ca(OH)_2$ in pure water = S mol/L

$$Ca(OH)_2 \rightleftharpoons \underset{S \text{ mol/L}}{Ca^{2+}} + \underset{2 \times S \text{ (mol/L)}}{2OH^-}$$

$$K_{sp} = [Ca^{2+}][OH^-]^2 = S \times (2S)^2$$
$$= 4S^3 \text{ (mol/L)}$$

The expression of K_{sp} can also be written as,

$$K_{sp} = x^x \cdot y^y \cdot S^{x+y}$$
$$= 1^1 \cdot 2^2 \cdot S^{1+2}$$
$$= 4S^3$$

[$\because$ For $Ca(OH)_2$: $x = 1, y = 2$]

x and y are the coefficients of cations and anions respectively

$$S = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{5.5 \times 10^{-6}}{4}\right)^{1/3}$$
$$= 1.11 \times 10^{-2} \text{ mol/L}$$

20 The solubility product of PbI_2 is 8.0×10^{-9}. The solubility of lead iodide in 0.1 molar solution of lead nitrate is $x \times 10^{-6}$ mol/L. The value of x is ..... (Rounded off to the nearest integer).

[Given, : $\sqrt{2} = 1.41$]

[2021, 24 Feb Shift-II]

Ans. ***(141)***

Given, $[K_{sp}]_{PbI_2} = 8 \times 10^{-9}$

To calculate solubility of PbI_2 in 0.1 M solution of $Pb(NO_3)_2$.

(I) $\underset{0.1 \text{ M}}{Pb(NO_3)_2} \longrightarrow \underset{0.1 \text{ M}}{Pb^{2+}(aq)} + \underset{0.2 \text{ M}}{2NO_3^-(aq)}$

(II) $PbI_2(s) \rightleftharpoons \underset{S}{Pb^{2+}(aq)} + \underset{2S}{2I^-(aq)}$

$\therefore \quad [Pb^{2+}] = S + 0.1 \approx 0.1$

$\because \quad S << 0.1$

Now, $K_{sp} = 8 \times 10^{-9}$

$[Pb^2][I^-]^2 = 8 \times 10^{-9}$

$$0.1 \times (2S)^2 = 8 \times 10^{-9}$$
$$4S^2 = 8 \times 10^{-8}$$
$$\Rightarrow \quad S = 141 \times 10^{-6} \text{ M}$$
$$x = 141$$

21 For the following Assertion and Reason, the correct option is

Assertion (A) When Cu (II) and sulphide ions are mixed, they react together extremely quickly to give a solid.

Reason (R) The equilibrium constant of $Cu^{2+}(aq) + S^{2-}(aq) \rightleftharpoons CuS(s)$ is high because the solubility product is low.

[2020, 2 Sep Shift-I]

(a) Both (A) and (R) are false.
(b) Both (A) and (R) are true and (R) is the explanation for (A).
(c) Both (A) and (R) are true but (R) is not the explanation for (A).
(d) (A) is false and (R) is true.

Ans. ***(c)***

Both (A) and (R) are correct, but (R) is not the correct explanation of (A).

[A] $Cu^{2+}(aq)$ and $S^{2-}(aq)$ ions undergo ionic reaction whose rate of reaction is very fast.

$$Cu^{2+}(aq) + S^{2-}(aq) \longrightarrow CuS\ (s) \downarrow$$

[R] For the reaction :

$$Cu^{2+}(aq) + S^{2-}(aq) \rightleftharpoons CuS(s)$$

The expression of equilibrium constant is,

$$K_{eq} = \frac{[CuS]}{[Cu^{2+}][S^{2-}]}$$

But, the expression of solubility product (K_{sp}) of $CuS(s)$ will be

$$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$$
$$K_{sp} = [Cu^{2+}][S^{2-}]$$

So, $K_{eq} = \frac{[CuS]}{K_{sp}}$ is, $K_{eq} \propto \frac{1}{K_{sp}}$

Because of high stability CuS, the value of K_{eq} is high, i.e. the value of K_{sp} of CuS will be low.

22 If the solubility product of AB_2 is 3.20×10^{-11} M^3, then the solubility of AB_2 in pure water is ..... $\times 10^4$ mol L^{-1}

[Assuming that neither kind of ion reacts with water]

[2020, 6 Sep Shift-II]

Ans. ***(2)***

$$AB_2(s) \rightleftharpoons A^{2+}(aq) + 2B^-(aq)$$

If the molar solubility of the solid substance is S mol L^{-1} then

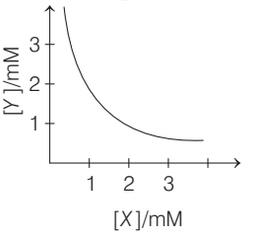
$$K_{sp} = [A^{2+}]^1[B^-]^2;$$
$$K_{sp} = S^1 \times (2S)^2 = 4S^3$$

Solubility product of $AB_2 = 3.20 \times 10^{-11}$ M^3

$$3.20 \times 10^{-11} = 4 \times S^3$$
$$\Rightarrow \quad S^3 = \frac{3.20 \times 10^{-11}}{4};$$
$$S = \left(\frac{3.20 \times 10^{-11}}{4}\right)^{1/3}$$
$$\Rightarrow \quad S = 2 \times 10^{-4} \text{ mol } L^{-1}$$

23 The stoichiometry and solubility product of a salt with the solubility curve given below is, respectively :

[2020, 8 Jan Shift-I]



(a) $X_2Y, 2 \times 10^{-9}$ M^3 (b) $XY, 2 \times 10^{-6}$ M^3
(c) $XY_2, 1 \times 10^{-9}$ M^3 (d) $XY_2, 4 \times 10^{-9}$ M^3

Ans. ***(d)***

Units given for all options is M^3, or $(\text{mol } L^{-1})^3$, which implies that, the equilibrium has three ions. Therefore,

$$XY_2 \rightleftharpoons X^{2+}(aq) + 2Y^-(aq), \quad K_{sp} = [X^{2+}][Y^-]^2$$

or $X_2Y \rightleftharpoons 2X^+(aq) + Y^{2-}(aq), \quad K_{sp} = [X^+]^2[Y^{2-}]$

(i) K_{sp} in case of XY_2,

$K_{sp} = (1 \times 10^{-3})(2 \times 10^{-3})^2 = 4 \times 10^{-9}$ M^3

(ii) K_{sp} in case of X_2Y,

$K_{sp} = (1 \times 10^{-3})^2 (2 \times 10^{-3}) = 2 \times 10^{-9}$ M

The only matching value of K_{sp} from options that satisfies the concentration values from graph is

$[X^{2+}] = 1 \text{ mM} = 1 \times 10^{-3}$ M

and $[Y^-] = 2 \times 10^{-3}$ M

Thus, salt is XY_2 and

$K_{sp} = (10^{-3})(2 \times 10^{-3})^2 = 4 \times 10^{-9}$ M^3

24 The K_{sp} for the following dissociation is 1.6×10^{-5}

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

Which of the following choices is correct for a mixture of 300 mL 0.134 M $Pb(NO_3)_2$ and 100 mL 0.4 M NaCl?

[2020, 9 Jan Shift-I]

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(a) $Q < K_{sp}$
(b) $Q > K_{sp}$
(c) $Q = K_{sp}$
(d) Not enough data provided

Ans. ***(b)***

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq); \quad K_{sp} = 1.6 \times 10^{-5}$$

For mixture, 300 mL 0.134 M $Pb(NO_3)_2$ and 100 mL 0.4 M NaCl

After mixing, total volume = 400 mL

$[Pb^{2+}]$ after mixing (before any precipitate forms)

$$= \frac{300 \times 0.134}{400} = \frac{3 \times 0.134}{4} \approx \frac{1}{10}$$

$[Cl^-]$ after mixing (before any precipitate forms)

$$= \frac{100 \times 0.4}{400} = 0.1$$

As we know,

$$Q = [Pb^{2+}][Cl^-]^2 = \frac{3 \times 0.134}{4} \times 10^{-2} \approx 10^{-3}$$

25 The solubility product of $Cr(OH)_3$ at 298 K is 6.0×10^{-31}. The concentration of hydroxide ions in a saturated solution of $Cr(OH)_3$ will be **[2020, 9 Jan Shift-II]**

(a) $(2.22 \times 10^{-31})^{1/4}$ (b) $(18 \times 10^{-31})^{1/4}$
(c) $(4.86 \times 10^{-29})^{1/4}$ (d) $(18 \times 10^{-31})^{1/2}$

Ans. ***(d)***

K_{sp} of $Cr(OH)_3$ at 298 K is 6.0×10^{-31}.

$[OH^-]$ in saturated solution of $Cr(OH)_3$ = ?

$$Cr(OH)_3 \rightleftharpoons \underset{S}{Cr^{3+}} + \underset{S}{3OH^-}$$

In a saturated solution,

$$K_{sp} = [Cr^{3+}][OH^-]^3$$
$$= S(3S)^3 = 27S^4 = 6.0 \times 10^{-31}$$
$$\therefore \quad S^4 = \frac{6.0 \times 10^{-31}}{27}$$
$$\Rightarrow \quad S = \left(\frac{6.0 \times 10^{-31}}{27}\right)^{\frac{1}{4}}$$
$$[OH]^- = 3S = 3\left(\frac{6.0 \times 10^{-31}}{27}\right)^{\frac{1}{4}}$$
$$= \left(\frac{6.0 \times 3^4}{3^3} \times 10^{-31}\right)^{\frac{1}{4}} = (18 \times 10^{-31})^{\frac{1}{4}}$$

26 If solubility product of $Zr_3(PO_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct? **[2019, 8 April Shift-I]**

(a) $S = \left(\frac{K_{sp}}{144}\right)^{1/6}$ (b) $S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$
(c) $S = \left(\frac{K_{sp}}{929}\right)^{1/9}$ (d) $S = \left(\frac{K_{sp}}{216}\right)^{1/7}$

Ans. ***(b)***

Key Idea The concentration of a substance in a saturated solution is defined as its solubility (S).

For $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$;

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

For, $Zr_3(PO_4)_4$,

$$Zr_3(PO_4)_4(s) \rightleftharpoons \underset{3S\,M}{3Zr^{4+}}(aq) + \underset{4\,S\,M}{4PO_4^{3-}}(aq)$$

$$K_{sp} = [Zr^{4+}]^3 [PO_4^{3-}]^4$$

$$K_{sp} = (3S)^3(4S)^4 = 6912\,S^7 \text{ or } S = \left(\frac{K_{sp}}{6912}\right)^{\frac{1}{7}}$$

Thus, the relation between molar solubility (S) and solubility product (K_{sp}) will be $S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$

27 What is the molar solubility of $Al(OH)_3$ in 0.2 M NaOH solution? Given that, solubility product of $Al(OH)_3 = 2.4 \times 10^{-24}$ **[2019, 12 April Shift-I]**

(a) 3×10^{-19} (b) 12×10^{-21}
(c) 3×10^{-22} (d) 12×10^{-23}

Ans. ***(c)***

Key Idea Concentration of substance in a saturated solution is defined as its solubility (S). Its value depends upon the nature of solvent and temperature. For reaction,

$$AB \rightleftharpoons A^+ + B^-$$
$$K_{sp} = [A^+][B^-]$$

$$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$$

Initially	1	0	0
At equilibrium	$1-S$	S	$3S+0.2$

$$NaOH \longrightarrow \underset{0.2}{Na^+} + \underset{0.2}{OH^-}$$

K_{sp} of $Al(OH)_3 = 2.4 \times 10^{-24}$ (Given)

$$K_{sp} = [Al^{3+}][OH^-]^3$$
$$2.4 \times 10^{-24} = [S][3S + 0.2]^3 \quad [\because 0.2 >> S]$$
$$2.4 \times 10^{-24} = [S][0.008]$$
$$[S] = 3 \times 10^{-22}$$

28 If K_{sp} of Ag_2CO_3 is 8×10^{-12}, the molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is **[2019, 12 Jan Shift-II]**

(a) 8×10^{-12} M (b) 8×10^{-13} M
(c) 8×10^{-10} M (d) 8×10^{-11} M

Ans. ***(c)***

Let the solubility of Ag_2CO_3 is S. Now, 0.1 M of $AgNO_3$ is added to this solution after which let the solubility of Ag_2CO_3 becomes S'.

$$\therefore \quad [Ag^+] = S + 0.1 \text{ and } [CO_3^{2-}] = S'$$
$$K_{sp} = (S + 0.1)^2 (S') \quad \ldots(i)$$

Given, $K_{sp} = 8 \times 10^{-12}$

$\because K_{sp}$ is very small, we neglect S' against S in Eq. (i)

$$\therefore \quad K_{sp} = (0.1)^2 S'$$
$$\text{or} \quad 8 \times 10^{-12} = 0.01\,S'$$
$$\text{or} \quad S' = 8 \times 10^{-12} \times 10^2$$
$$= 8 \times 10^{-10} \text{ M}$$

Thus, molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is 8×10^{-10} M.

29 An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is : **[JEE Main 2018]**

(a) 5×10^{-8} (b) 3×10^{-20}
(c) 6×10^{-21} (d) 5×10^{-19}

Ans. ***(b)***

Given,

$[H_2S] = 0.10$ M

$[HCl] = 0.20$ M So, $[H^+] = 0.20$ M

$$H_2S \rightleftharpoons H^+ + HS^-, K_1 = 1.0 \times 10^{-7}$$
$$HS^- \rightleftharpoons H^+ + S^{2-}, K_2 = 1.2 \times 10^{-13}$$

It means for,

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
$$K = K_1 \times K_2$$
$$= 1.0 \times 10^{-7} \times 1.2 \times 10^{-13}$$
$$= 1.2 \times 10^{-20}$$

Now $[S^{2-}] = \frac{K \times [H_2S]}{[H^+]^2}$ [according to the final equation]

$$= \frac{1.2 \times 10^{-20} \times 0.1\text{ M}}{(0.2\text{M})^2}$$
$$= \frac{1.2 \times 10^{-20} \times 1 \times 10^{-1}\text{ M}}{4 \times 10^{-2}\text{M}}$$
$$= 3 \times 10^{-20} \text{ M}$$

30 An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}.

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What is the original concentration of Ba^{2+}? **[JEE Main 2018]**

(a) 5×10^{-9} M (b) 2×10^{-9} M
(c) 1.1×10^{-9} M (d) 1.0×10^{-10} M

Ans. *(c)*

Its given that the final volume is 500 mL and this final volume was arrived when 50 mL of 1 M Na_2SO_4 was added to unknown Ba^{2+} solution.

So, we can interpret the volume of unknown Ba^{2+} solution as 450 mL i.e.

$$\underset{Ba^{2+}\text{ solution}}{450\text{mL}} + \underset{Na_2SO_4\text{ solution}}{50\text{mL}} \longrightarrow \underset{BaSO_4\text{ solution}}{500\text{mL}}$$

From this we can calculate the concentration of SO_4^{2-} ion in the solution *via*

$$M_1V_1 = M_2V_2$$
$$1\times50 = M_2\times500$$

(as 1M Na_2SO_4 is taken into consideration)

$$M_2 = \frac{1}{10} = 0.1\text{M}$$

Now for just precipitation,

Ionic product = Solubility product (K_{sp})

i.e. $[Ba^{2+}][SO_4^{2-}] = K_{sp}$ of $BaSO_4$

Given K_{sp} of $BaSO_4 = 1\times10^{-10}$

So, $[Ba^{2+}][0.1] = 1\times10^{-10}$

or $[Ba^{2+}] = 1\times10^{-9}$ M

Remember This is the concentration of Ba^{2+} ions in final solution.

Hence, for calculating the $[Ba^{2+}]$ in original solution we have to use

$$M_1V_1 = M_2V_2$$

as $M_1\times450 = 10^{-9}\times500$

so, $M_1 = 1.1\times10^{-9}$M

31 The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is **[AIEEE 2011]**

(a) $\sqrt[2]{1.6\times10^{-30}}$

(b) $\sqrt[4]{1.6\times10^{-30}}$

(c) $\sqrt[4]{1.6\times10^{-30}/27}$

(d) $1.6\times10^{-30}/27$

Ans. *(c)*

Let molar solubility of $Cr(OH)_3$ = s mol L^{-1}

$$Cr(OH)_3(s) \rightleftharpoons \underset{s}{Cr^{3+}}(aq) + \underset{3s}{3OH^-}(aq)$$

$$K_{sp} = 1.6\times10^{-30} = [Cr^{3+}][OH^-]^3 = (s)(3s)^3 = 27s^4$$

$$\therefore\quad s^4 = \frac{1.6\times10^{-30}}{27}$$

$$\Rightarrow\quad s = \sqrt[4]{\frac{1.6\times10^{-30}}{27}}$$

32 Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **[AIEEE 2010]**

(a) 1.2×10^{-10} g (b) 1.2×10^{-9} g
(c) 6.2×10^{-5} g (d) 5.0×10^{-8} g

Ans. *(b)*

$$[AgBr] = [Ag^+] = 0.05\text{ M}$$

$$K_{sp}\,[AgBr] = [Ag^+][Br^-]$$

$$\Rightarrow\quad [Br^-] = \frac{K_{sp}\,(AgBr)}{[Ag^+]}$$

$$= \frac{5.0\times10^{-13}}{0.05} = 10^{-11}\,[\text{mol L}^{-1}]$$

Moles of KBr needed to precipitate AgBr

$= [Br^-]\times V = 10^{-11}$ mol $L^{-1}\times1$ L $= 10^{-11}$ mol

Therefore, amount of KBr needed to precipitate AgBr

$= 10^{-11}$ mol $\times$ 120 g $mol^{-1} = 1.2\times10^{-9}$ g

33 Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+}, will a precipitate begin to form? (K_{sp} for $BaCO_3 = 5.1\times10^{-9}$) **[AIEEE 2009]**

(a) 4.1×10^{-5} M (b) 5.1×10^{-5} M
(c) 8.1×10^{-8} M (d) 8.1×10^{-7} M

Ans. *(b)*

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$$

$$[Na_2CO_3] = [CO_3^{2-}] = 1\times10^{-4}\text{ M}$$

$$BaCO_3 \rightleftharpoons Ba^{2+}\ CO_3^{2-}$$

$$K_{sp(BaCO_3)} = [Ba^{2+}][CO_3^{2-}]$$

$$[Ba^{2+}] = \frac{K_{sp}\,(BaCO_3)}{[CO_3^{2-}]}$$

$$\Rightarrow\quad [Ba^{2+}] = \frac{5.1\times10^{-9}}{1\times10^{-4}}$$

$$[Ba^{2+}] = 5.1\times10^{-5}\text{ M}$$

Hence, at 5.1×10^{-5} M concentration of Ba^{2+}, a precipitate will begin to form.

34 In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is

$$AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$$

If the solubility product constant, K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution? **[AIEEE 2007]**

(a) 28.3×10^{-2} g (b) 2.83×10^{-3} g
(c) 1.0×10^{-7} g (d) 1.0×10^{-4} g

Ans. *(b)*

$$AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$$

Let the solubility of $AgIO_3$ be S

$$K_{sp} = [Ag^+][IO_3^-]$$

$$1.0\times10^{-8} = S^2 \quad \text{or} \quad S = 1\times10^{-4}\text{ mol/L}$$

In 1000 mL moles of $AgIO_3$ dissolved $= 1\times10^{-4}$ moles

In 100 mL moles of $AgIO_3$ dissolved $= 1\times10^{-5}$ moles

Mass of $AgIO_3$ in 100 mL

$= 1\times10^{-5}$ mol $\times 283$ g mol^{-1}

$= 2.83\times10^{-3}$ g

35 The solubility product of a salt having general formula MX_2, in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **[AIEEE 2005]**

(a) 4.0×10^{-10} M (b) 1.6×10^{-4} M
(c) 1.0×10^{-4} M (d) 2.0×10^{-6} M

Ans. *(c)*

$$MX_2 \rightleftharpoons \underset{S}{M^{2+}} + \underset{2S}{2X^-}$$

$$K_{sp} = [M^{2+}][X^-]^2$$

If solubility be S, then

$$K_{sp} = (S)(2S)^2 = 4S^3$$

$$4S^3 = 4\times10^{-12} \Rightarrow S = 1\times10^{-4}\text{ M}$$

$$\therefore\quad [M^{2+}] = S = 1\times10^{-4}\text{ M}$$

36 The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is S. The corresponding solubility product is K_{sp}. S is given in terms of K_{sp} by the relation.

(a) $S = (K_{sp}/128)^{1/4}$ (b) $S = (K_{sp}/128)^{1/4}$
(c) $S = (K_{sp}/256)^{1/5}$ (d) $S = (K_{sp}/256)^{1/5}$ **[AIEEE 2004]**

Ans. *(c)*

$$MX_4 \rightleftharpoons M^{4+} + 4X^-$$

$$K_{sp} = [M^{4+}][4X^-]^4$$

$$K_{sp} = (S)(4S)^4$$

$$\Rightarrow\quad K_{sp} = 256\,S^5$$

$$S^5 = \frac{K_{sp}}{256}$$

$$\Rightarrow\quad S = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

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37 The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product will be **[AIEEE 2003]**

(a) 4×10^{-15} (b) 4×10^{-10}

(c) 1×10^{-15} (d) 1×10^{-10}

Ans. ***(a)***

$$AB_2 \rightleftharpoons \underset{S}{A^{2+}} + \underset{2S}{2B^-}$$

$$K_{sp} = [A^{2+}][B^-]^2 = (S)(2S)^2 = 4S^3$$
$$= 4(1\times10^{-5})^3 = 4\times10^{-15}$$

38 Solubility of $Ca(OH)_2$ is S mol L^{-1}. The solubility product (K_{sp}) under the same condition is **[AIEEE 2002]**

(a) $4S^3$ (b) $3S^4$ (c) $4S^2$ (d) S^3

Ans. ***(a)***

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$
$$K_{sp} = [Ca^{2+}][OH^-]^2 = (S)(2S)^2 = 4S^3$$

TOPIC 4
pH, Buffer and Indicator

39 The pH of a solution obtained by mixing
50 mL of 1 M HCl and 30 mL of 1 M NaOH is $x\times10^{-4}$. The value of x is ..... (Nearest integer)
[log 2.5 = 0.3979]
[2021, 31 Aug Shift-II]

Ans. ***(6021)***

Milliequivalents of HCl
$(N_aV_a) = 50\times1 = 50$
Milliequivalents of NaOH
$(N_bV_b) = 30\times1 = 30$
Since, $N_aV_a > N_bV_b$
and they neutralise each other

$$[H^+] = \frac{N_aV_a - N_bV_b}{V_a + V_b}$$
$$= \frac{50-30}{80} = 0.25 = 2.5\times10^{-1}$$
$$pH = -\log[H^+]$$
$$= -\log(2.5\times10^{-1})$$
$$= 1 - 0.3979 = 0.6021$$
$$pH\times10^4 = 0.6021\times10^4 = 6021$$
$$\therefore \quad x = 6021$$

40 In order to prepare a buffer solution of pH 5.74, sodium acetate is added to acetic acid. If the concentration of acetic acid in the buffer is 1.0 M, the concentration of sodium acetate in the buffer is ..... M. (Round off to the nearest integer).
[Given : pK_a (acetic acid) = 4.74]
[2021, 18 March Shift-I]

Ans. ***(10)***

Given : pH = 5.74
Concentration of acetic acid in buffer = 1.0 M
Acetic acid and its conjugate base sodium acetate makes acidic buffer.
$CH_3COOH + CH_3COONa \longrightarrow$ (Acidic buffer)
Using formula,

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$
$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$
$$5.74 = 4.74 + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$
$$5.74 - 4.74 = \log\frac{[CH_3COONa]}{[CH_3COOH]}$$
$$1 = \log\frac{[CH_3COONa]}{[CH_3COOH]}$$
$$\Rightarrow \quad \frac{[CH_3COONa]}{[CH_3COOH]} = 10 \qquad [\because [CH_3COOH] = 1]$$

$[CH_3COONa] = [10\times1] = 10$
Thus, the concentration of sodium acetate in buffer is 10 M.

41 Sulphurous acid (H_2SO_3) has $K_{a_1} = 1.7\times10^{-2}$ and $K_{a_2} = 6.4\times10^{-8}$. The pH of 0.588 M is .....
(Round off to the nearest integer)
[2021, 16 March Shift-II]

Ans. ***(1)***

For H_2SO_3, $K_{a_1} >> K_{a_2}$
So, we mainly consider 1st ionisation

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-;\ K_{a_1} = 1.7\times10^{-2}$$

$t = 0$	0.558	0	0
$t = t_{eq}$	$0.558 - 0.558\alpha$	0.558α	0.558α

$$K_{a_1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]}$$
$$= \frac{(0.558\alpha)(0.558\alpha)}{0.558(1-\alpha)} = \frac{0.558\alpha^2}{1-\alpha}$$

$\alpha << 1$ for weak acid
$(1-\alpha) \approx 1$

$$\alpha = \sqrt{\frac{K_{a_1}}{0.558}} = \sqrt{\frac{1.7\times10^{-2}}{0.558}}$$
$$\alpha = 1.7\times10^{-1} = 0.17$$
$$[H]^+ = 0.558\alpha = 9.9\times10^{-2}$$
$$pH = -\log[H^+] = -\log(9.9\times10^{-2}) \qquad [\because \log 9.9 \approx 1]$$
$$= 2 - \log 9.9 = 2 - 1$$
$$pH = 1$$

42 The pH of ammonium phosphate solution, if pK_a of phosphoric acid and pK_b of ammonium hydroxide are 5.23 and 4.75 respectively, is ..... . **[2021, 26 Feb Shift-II]**

Ans. ***(7)***

Phosphoric acid is a weak tribasic acid (H_3PO_4) and NH_4OH is a weak monoacidic base. So, hydrolysis of ammonium phosphate $(NH_4)_3PO_4$ can be shown as,
$(NH_4)_3PO_4 + 3H_2O \rightleftharpoons H_3PO_4 + 3NH_4OH$
[3 : 1 type salt]

$$\text{So,} \quad [H^+] = K_a\times\left(\frac{K_w}{K_a\times K_b}\right)^{12}$$
$$pH = pK_a + \frac{1}{2}[pK_w - pK_a - pK_b]$$
$$= 5.23 + \frac{1}{2}(14 - 5.23 - 4.75) \qquad [\because pK_w = 14 H_2O$$
$$pK_a = 5.23\ (H_3PO_4)$$
$$pK_b = 4.75\ (NH_4OH)] = 7.24 \simeq 7$$

43 The solubility of AgCN in a buffer solution of pH = 3 is x. The value of x is..... .
[Assume : No cyano complex is formed; $K_{sp}(AgCN) = 2.2\times10^{-16}$ and $K_a(HCN) = 6.2\times10^{-10}$]
[2021, 25 Feb Shift-I]

(a) 0.625×10^{-6} (b) 1.6×10^{-6}

(c) 2.2×10^{-16} (d) 1.9×10^{-5}

Ans. ***(d)***

pH of AgCN buffer solution = 3

$$[H^+] = 10^{-3}$$
$$K_{sp}(AgCN) = 2.2\times10^{-16}$$
$$K_a[HCN] = 6.2\times10^{-10}$$
$$AgCN \rightleftharpoons Ag^+ + CN^- \ldots\ldots K_{sp}$$
$$CN^- + H^+ \rightleftharpoons HCN \ldots\ldots \frac{1}{K_a}$$
$$AgCN + H^+ \rightleftharpoons HCN + Ag^+$$
$$K_{sp}\times\frac{1}{K_a} = \frac{[Ag^+][CN^-][HCN]}{[H^+][CN^-]}$$
$$[S] = \sqrt{\frac{K_{sp}[H^+]}{K_a}}$$
$$\Rightarrow \quad \frac{2.2\times10^{-16}}{6.2\times10^{-10}} = \frac{[S][S]}{10^{-3}}$$
$$[S]^2 = \frac{2.2\times10^{-16}}{6.2\times10^{-10}}\times10^{-3}$$
$$S = 1.9\times10^{-5}$$

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44 An acidic buffer is obtained on mixing **[2020, 3 Sep Shift-I]**

(a) 100 mL of 0.1 M CH_3COOH and 100 mL of 0.1 M NaOH

(b) 100 mL of 0.1 M HCl and 200 mL of 0.1 M NaCl

(c) 100 mL of 0.1 M CH_3COOH and 200 mL of 0.1 M NaOH

(d) 100 mL of 0.1 M HCl and 200 mL of 0.1 M CH_3COONa

Ans. ***(d)***

An acidic buffer is a mixture of weak acid and its salt with strong base. Now, let us study the composition of each mixture obtained by mixing of two solutions.

(a) $CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$

millimol					
$t=0$	100×0.1	100×0.1	0	0
$t=a$	0	0	10	10

So, it is not a buffer.

NaCl, a salt of strong acid (HCl) and strong base (NaOH) is not hydrolisable by HCl also. So, it is not a buffer.

$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$

millimol					
$t=0$	100×0.1 (Limiting)	200×0.1	0	0
$t=a$	0	$20-10=10$	10	10

After mixing, the solution contains equimolar amounts by NaOH (a strong base) and $CH_3COO^-Na^+$ (salt).

So, it is also not a buffer.

$CH_3COO^-Na^+ + HCl \longrightarrow CH_3COOH + NaCl$

millimol					
$t=0$	200×0.1	100×0.1 (Limiting)	0	0
$t=a$	$20-10=10$	0	10	10

Now, the resultant solution contains equimolar amount of CH_3COOH (an weak acid) and CH_3COONa (a salt of CH_3COOH with a strong base, NaOH).

So, it is an acid buffer.

45 100 mL of 0.1M HCl is taken is a beaker and to it 100 mL of 0.1 M NaOH is added in steps of 2 mL and the pH continuously measured. Which of the following graphs correctly depicts the change in pH? **[2020, 3 Sep Shift-II]**

(a) pH 7 — vol. of NaOH

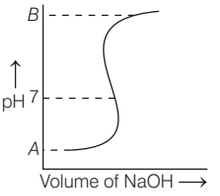
(b) pH 7 — vol. of NaOH

(c) pH 7 — vol. of NaOH

(d) pH 7 — vol. of NaOH

Ans. ***(a)***

Given 100 mL of 0.1 M HCl is taken in beaker and to it 100 mL of 0.1 M NaOH is added.



This is acid (HCl) and base (NaOH) titration. Here, phenolphthalein act as an indicator and colour change is pink. The correct graph that depicts the change in pH is as follows.

At first HCl (acid) is take in beaker and base (NaOH) is taken in burette.

When base is added drop wise then acid-base reaction is occurs and following changes are observed.

pH → 0 to 7 is acidic. pH → 7 is neutral.

pH → 7 to 14 is basic.

Initially, the graph increases steeply but when concentration of acid becomes equal to base then no change is seen in graph.

This point is called neutral point or equivalence point. Equivalence point, where pH = 7.

After the equivalence point (pH = 7), base (NaOH) is continuously mixed drop by drop then pH increases by 7 and graph also increases slowly. At the point *B*, solution become basic, again base (NaOH) is mixed drop by drop and the solution becomes basic at point *B*. Following inference can be seen in the graphs.

(a) According to this graph, pH = 7 is equivalence point and use of NaOH (base) drop by drop leads to basic solution as a result, value of pH increases slowly. This is correct option.

(b) According to graph, it shows straight line that mean graph increases instantly but this titration show pH increases slowly because base (NaOH) is mix drop by drop.

(c) After equivalence point (pH = 7) graph is constant. It is wrong because graph increases and the solution becomes pure basic then graph show constant value.

(d) According to graph, equivalence point (pH = 7) graph should increase but it decreases.

46 A soft drink was bottled with a partial pressure of CO_2 of 3 bar over the liquid at room temperature. The partial pressure of CO_2 over the solution approaches a value of 30 bar when 44 g of CO_2 is dissolved in 1 kg of water at room temperature. The approximate pH of the soft drink is ..... $\times10^{-1}$.

(First dissociation constant of $H_2CO_3 = 4.0\times10^{-7}$) $\log2 = 0.3$; density of the soft drink = 1g mL^{-1})

[2020, 6 Sep Shift-I]

Ans. ***(37)***

At 30 bar pressure mass of CO_2 in 1 kg water = 44 g

At 3 bar pressure mass of CO_2 in 1 kg water = 4.4 g

Moles of CO_2 in 1 kg water $= \frac{4.4}{44} = 0.1\,\text{mol}$

In solution, $H_2O + CO_2 \rightleftharpoons H_2CO_3$ (0.1 mol)

or $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

Initially	0.1	–	–
At equil.	$0.1(1-\alpha)$	0.1α	0.1α

Here, α = degree of dissociation

$$K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

[Here, K_{a_1} = first dissociation of constant of H_2CO_3]

$$4\times10^{-7} = \frac{(0.1\alpha)^2}{0.1(1-\alpha)} = 0.1\alpha^2 \qquad \left[\because \frac{K_a}{C} < 10^{-3},\ 1-\alpha \cong 1\right]$$

$4.0\times10^{-7}\times0.1 = 0.01\alpha^2$; $\alpha = 2\times10^{-3}$

$[H^+] = 0.1\alpha = 0.1\times2\times10^{-3}$

$= 2\times10^{-4}$

$pH = -\log[H^+]$

$= -\log[2\times10^{-4}]$

$= -[\log2 + \log[10^{-4}]]$

$= -[0.3-4]$

$= 3.7 = 37\times10^{-1}$

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47 3 g of acetic acid is added to 250 mL of 0.1 M HCl and the solution made up to 500 mL. To 20 mL of this solution $\frac{1}{2}$ mL of 5 M NaOH is added. The pH of the solution is .....

[Given : pK_a of acetic acid = 4.75, molar mass of acetic acid = 60 g/mol, log 3 = 0.4771]

Neglect any changes in volume.

[2020, 7 Jan Shift-II]

Ans. ***(5.23)***

3g $CH_3COOH(M=60) = \frac{3}{60} = \frac{1}{20}$ mol

250 mL of 0.1 M HCl = $M \times V = \frac{250}{1000} \times 0.1$

$= 25 \times 10^{-3}$ mol

After mixing these two, solution is diluted to 500 mL.

Then from that solution, 20 mL is taken.

Number of moles of both CH_3COOH and HCl will be now only $\frac{20}{500} = \frac{1}{25}$ of original solution.

$$n_{CH_3COOH} = \frac{1}{20} \times \frac{1}{25} = \frac{1}{500} = 2 \times 10^{-3} \text{ mol}$$

$$n_{HCl} = 25 \times 10^{-3} \times \frac{1}{25} = 10^{-3} \text{ mol}$$

$$n_{NaOH} \text{ added} = M \times V = \frac{1}{2} \times 5 \times 10^{-3}$$

$$= 2.5 \times 10^{-3}$$

After mixing, all HCl and NaOH will be neutralised. Remaining number of moles.

$n_{NaCl} = 10^{-3}$

$n_{CH_3COONa} = 1.5 \times 10^{-3}$

n_{CH_3COOH} (unreacted) $= 0.5 \times 10^{-3}$

∴ Now the solution is a buffer solution.

$$pH = pK_a = \log \frac{[salt]}{[acid]}$$

$$= pK_a + \log \frac{(n_{CH_3COONa})}{(n_{CH_3COOH})}$$

$$= 4.75 + \log 3 = 4.75 + 0.4771$$

$$= 5.2271 \approx 5.23$$

48 Arrange the following solutions in the decreasing order of pOH.

(A) 0.01 M HCl (B) 0.01 M NaOH

(C) 0.01 M CH_3COONa

(D) 0.01 M NaCl **[2020, 6 Sep Shift-I]**

(a) (A) > (C) > (D) > (B)

(b) (A) > (D) > (C) > (B)

(c) (B) > (C) > (D) > (A)

(d) (B) > (D) > (C) > (A)

Ans. ***(b)***

(A) pOH of 0.01 M HCl :

$$\underset{(0.01M)}{HCl} \longrightarrow \underset{(0.01M)}{H^+} + \underset{(0.01M)}{OH^-}$$

$[H^+] = (0.01M)$; $pH = -\log [H^+]$

$\Rightarrow -\log(10^{-2}) \Rightarrow 2$

$\therefore pOH = 14 - pH \Rightarrow 14 - 2 = 12$

(B) pOH of 0.01 M NaOH :

$$\underset{(0.01M)}{NaOH} \longrightarrow \underset{(0.01M)}{Na^+} + \underset{(0.01M)}{OH^-}$$

$[OH^-] = 10^{-2}$

$\therefore \quad pOH = -\log [OH^-]$

$\Rightarrow \quad -\log(10^{-2}) = 2$

(C) pOH of 0.01 M $CH_3\overset{-}{C}OO\overset{+}{N}a$:

(salt of weak acid + strong base)

$$pH = 7 + \frac{1}{2}[pK_a + \log(10^{-2})]$$

$\therefore$ pH > 7, thus pOH < 7

(D) pOH of 0.01 M NaCl :

(It is a salt of strong acid + strong base)

$\therefore \quad pH = pOH \Rightarrow 7$

Thus, order of pOH value :

(A) > (D) > (C) > (B)

Hence, the correct option is (b).

49 Two solutions, *A* and *B*, each of 100 L was made by dissolving 4 g of NaOH and 9.8 g of H_2SO_4 in water, respectively. The pH of the resultant solution obtained from mixing 40 L of solution *A* and 10 L of solution *B* is ..... .

[2020, 7 Jan Shift-I]

Ans. ***(10.60)***

(A) 4 g NaOH in 100 L

$$\Rightarrow \quad M = \frac{4/40}{100} = 10^{-3} \text{ mol L}^{-1}.$$

(B) 9.8 g H_2SO_4 in 100 L

$$\Rightarrow \quad M = \frac{9.8/98}{100} = 10^{-3} \text{ mol L}^{-1}$$

40 L of solution *A* contains

$= 40 \times 10^{-3}$ mol NaOH $\quad (\because n = M \times V)$

$= 40 \times 10^{-3}$ mol OH^-

10 L of solution *B* contains

$= 10 \times 10^{-3}$ mol H_2SO_4

$= 20 \times 10^{-3}$ mol H^+

When they are mixed, total volume = 50 L and all H^+ is neutralised by OH^-.

Number of moles (n_{OH^-}) of excess OH^-.

$$= (40 - 20) \times 10^{-3} = 20 \times 10^{-3}$$

$$[OH^-] = \frac{n_{OH^-}}{V_{solution}} \text{ (in litre)}$$

Or $$[OH^-] = \frac{n_{OH^-}}{\text{Total volume}}$$

$$= \frac{20 \times 10^{-3}}{50} = 4 \times 10^{-4} \text{ M}$$

As we know,

$pOH = -\log[OH^-]$

$\therefore \quad pOH = -\log 4 \times 10^{-4} = 4 - \log 4$

or $\quad pH = 14 - pOH$

$= 14 - (4 - \log 4)$

$= 10 + \log 4 = 10.602$

50 The strength of an aqueous NaOH solution is most accurately determined by titrating : (Note : consider that an appropriate indicator is used) **[2020, 8 Jan Shift-I]**

(a) Aq. NaOH in a volumetric flask and concentrated H_2SO_4 in a conical flask

(b) Aq. NaOH in a pipette and aqueous oxalic acid in a burette

(c) Aq. NaOH in a burette and aqueous oxalic acid in a conical flask

(d) Aq. NaOH in a burette and concentrated H_2SO_4 in a conical flask

Ans. ***(c)***

The strength of aqueous NaOH solution is most accurately determined by titrating aqueous NaOH in burette and aqueous oxalic acid in conical flask with phenolphthalein as an indicator. (For weak acid-strong base titration, methyl orange cannot be used).

Thus, solution turns colourless to pink at the end point. (Phenolphthalein has pink colour when pH > 10 and it is colourless when pH < 8 (approximately) which is easily to perceive.

If NaOH is taken in conical flask and oxalic acid is added from burette, the end point will be the decolourisation of pink colour which is more difficult to percieve by human eye very quickly.

51 For the following Assertion and Reason, the correct option is

Assertion (A) The pH of water increases with increase in temperature.

Reason (R) The dissociation of water into H^+ and OH^- is an exothermic reaction.

[2020, 8 Jan Shift-II]

(a) Assertion is not true, but Reason is true.

(b) Both assertion and Reason are true and the Reason is the correct explanation for the Assertion.

(c) Both Assertion and Reason are false.

(d) Both Assertion and Reason are true, but the Reason is not the correct explanation for the Assertion.

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Ans. *(c)*

The dissociation of water into H^+ and OH^- is an endothermic reaction.

$\therefore$ As temperature increases, its equilibrium constant also increases.

$\therefore [H^+]$ and $[OH^-]$ in water at equilibrium increases with increase in temperature.

$\therefore$ $pH = -\log[H^+]$ decreases, as temperature increases.

So, both Assertion and Reason are false.

52 The molar solubility of $Cd(OH)_2$ is 1.84×10^{-5} m in water. The expected solubility of $Cd(OH)_2$ in a buffer solution of pH = 12 is

[2019, 12 April Shift-I]

(a) 1.84×10^{-9} M

(b) $\frac{2.49}{1.84} \times 10^{-9}$ M

(c) 6.23×10^{-11} M

(d) 2.49×10^{-10} M

Ans. *(d)*

Key Idea The concentration of substance in a saturated solution is defined as its solubility (S). Its value depends upon the nature of solvent and temperature.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Solubility of

$$Cd(OH)_2 (S) = 1.84 \times 10^{-5} \text{ M}$$

Given, pH = 12 [for $Cd(OH)_2$ in buffer solution]

So, $pOH = 2$ ($\because pH + pOH = pK_w$)

$$12 + pOH = 14$$

$$pOH = 14 - 12 = 2$$

$\therefore$ $[OH^-] = 10^{-2}$ in buffer solution.

For reaction $Cd(OH)_2 \longrightarrow \underset{S}{Cd^{2+}} + \underset{S^2}{2OH^-}$

$$K_{sp} = [Cd^{2+}][OH^-]^2$$

$$K_{sp} = (S)(2S)^2 = 4S^3$$

$$= 4(1.84 \times 10^{-5})^3$$

$$K_{sp} = 24.9 \times 10^{-15}$$

$$[Cd^{2+}] = \frac{K_{sp}}{[OH^-]^2}$$

$$[Cd^{2+}] = \frac{24.9 \times 10^{-15}}{(10^{-2})^2}$$

$$= 24.9 \times 10^{-15} \times 10^{+4}$$

$$= 24.9 \times 10^{-11} \text{ M}$$

$[Cd^{2+}] \Rightarrow 2.49 \times 10^{-10}$ M

The expected solubility of $Cd(OH)_2$ in a buffer solution of pH = 12 is 2.49×10^{-10} M.

53 Consider the following statements.

I. The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.

II. Ionic product of water is temperature dependent.

III. A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.

IV. The Le-Chatelier's principle is not applicable to common-ion effect. The correct statements are

[2019, 10 April Shift-I]

(a) I, II and IV (b) II and III

(c) I and II (d) I, II and III

Ans. *(d)*

The explanation of given statements are as follows:

In statement (I), millimoles of H^+

$$= 400 \times 0.1 \times 2 = 80$$

Millimoles of $OH^- = 400 \times 0.1 = 40$ (Limiting reagent)

$\therefore$ Millimoles of H^+ left $= 80 - 40 = 40$

$$[H^+] = \frac{40}{400 + 400} = \frac{40}{800} M = \frac{1}{20} M$$

$$\Rightarrow \quad pH = -\log[H^+] = -\log\left(\frac{1}{20}\right)$$

$$= -\log 1 + \log 2 + \log 10$$

$$= -0 + 0.301 + 1 \Rightarrow 1.30$$

Hence, the option (a) is correct.

In statement (II), ionic product of H_2O is temperature dependent.

$K_w = [H^+][OH^-] \approx 10^{-14} (\text{mol/L})^2$ at 25ºC

With increase in temperature, dissociation of H_2O units into H^+ and OH^- ions will also increase. As a result, the value of ionic product, $[H^+] \times [OH^-]$ will be increased. e.g.

Temperature	K_w	L^2
5ºC	0.186×10^{-14}	
25ºC	1.008×10^{-14}	
45ºC	4.074×10^{-14}	

Hence, the option (b) is correct.

In statement (III), for a weak monobasic acid HA

$$\underset{(1-\alpha)C \text{ M}}{HA} \rightleftharpoons \underset{\alpha C \text{ M}}{H^{\oplus}} + \underset{\alpha C \text{ M}}{A^{\ominus}}$$

$\Rightarrow$ pH of the solution is 5, i.e.

$$[H^+] = 10^{-5} \text{ M} = \alpha C$$

$$\Rightarrow \quad K_a = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{10^{-5} \times \alpha}{1-\alpha}$$

$$\Rightarrow \quad 10^{-5} = \frac{10^{-5} \times \alpha}{1-\alpha}$$

$$\Rightarrow \quad \alpha = 0.5 \Rightarrow \alpha\% = 50$$

Hence, the option (c) is correct.

In statement (IV), Le-Chatelier's principle is applicable to common ion effect. Because, in presence of common ion (given) by strong electrolyte (say, $Na^+ \bar{A}$), the product of the concentration terms in RHS increases. For the weaker electrolyte, HA (say) the equilibrium shifts to the LHS, $HA \rightleftharpoons H^{\oplus} + A^{\ominus}$.

As a result dissociation of HA gets suppressed. Hence, the option (d) is incorrect.

54 20 mL of 0.1 M H_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is [pK_b of $NH_4OH = 4.7$]

(a) 9.3 (b) 5.0 (c) 9.0 (d) 5.2

[2019, 9 Jan Shift-I]

Ans. *(a)*

The reaction takes place when H_2SO_4 is added to NH_4OH is as follows :

$$\underset{\text{Strong acid}}{H_2SO_4} + 2\underset{\text{Weak base}}{NH_4OH} \longrightarrow \underset{\text{Salt of strong acid + weak base}}{(NH_4)_2SO_4} + 2H_2O$$

Millimoles at $t = 0$	$20 \times 0.1 = 2$	$30 \times 0.2 = 6$	0
Millimoles at $t = t$	0	2	2

So, the resulting solution is a basic buffer [$NH_4OH + (NH_4)_2SO_4$].

According to the Henderson's equation,

$$pOH = pK_b + \log \frac{[(NH_4)_2SO_4]}{[NH_4OH]}$$

$$= 4.7 + \log \frac{2}{2} = 4.7$$

$$\Rightarrow \quad pH = 14 - pOH$$

$$= 14 - 4.7 = 9.3$$

55 An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination? **[JEE Main 2018]**

	Base	Acid	End point
(a)	Weak	Strong	Colourless to pink
(b)	Strong	Strong	Pinkish red to yellow
(c)	Weak	Strong	Yellow to pinkish red
(d)	Strong	Strong	Pink to colourless

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Ans. *(c)*

Methyl orange show Pinkish colour towards more acidic medium and yellow orange colour towards basic or less acidic media. Its working pH range is

Weak base have the pH range greater than 7. When methyl orange is added to this weak base solution it shows yellow orange colour.

Now when this solution is titrated against strong acid the pH move towards more acidic range and reaches to end point near 3.9 where yellow orange colour of methyl orange changes to Pinkish red resulting to similar change in colour of solution as well.

56 pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is **[JEE Main 2017]**

(a) 7.2 (b) 6.9
(c) 7.0 (d) 1.0

Ans. *(b)*

For a salt of weak acid and weak base,

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

Given, $pK_a(HA) = 3.2$,

$pK_a(BOH) = 3.4$

$$\therefore \quad pH = 7 + \frac{1}{2}(3.2) - \frac{1}{2}(3.4)$$

$$= 7 + 1.6 - 1.7 = 6.9$$

57 How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **[JEE Main 2014]**

(a) 0.1 L (b) 0.9 L
(c) 2.0 L (d) 9.0 L

Ans. *(d)*

$pH = 1 \Rightarrow [H^+] = 10^{-1} = 0.1\ M$

$pH = 2 \Rightarrow [H^+] = 10^{-2} = 0.01\ M$

For dilution of HCl,

$$M_1V_1 = M_2V_2$$

$$0.1 \times 1 = 0.01 \times V_2$$

$$\Rightarrow \quad V_2 = 10\ L$$

Volume of water to be added $= 10 - 1 = 9\ L$

58 An acid HA ionises as

$HA \rightleftharpoons H^+ + A^-$

The pH of 1.0 M solution is 5. Its dissociation constant would be **[AIEEE 2011]**

(a) 1×10^{-10} (b) 5
(c) 5×10^{-8} (d) 1×10^{-5}

Ans. *(a)*

pH of a solution = 5

$$\therefore \quad [H^+] = 10^{-pH} = 10^{-5}$$

HA (a weak acid) ionises as

$$HA \rightleftharpoons H^+ + A^-$$

$$1.0 \quad 0 \quad 0$$

$$(1 - 10^{-5}) \quad 10^{-5} \quad 10^{-5}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{10^{-5} \times 10^{-5}}{(1 - 10^{-5})}$$

$$= \frac{10^{-10}}{1} \qquad [\because 1 >>> 10^{-5}]$$

$$= 1 \times 10^{-10}\ M$$

59 At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions? **[AIEEE 2010]**

(a) 9 (b) 10
(c) 11 (d) 8

Ans. *(b)*

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1 \times 10^{-11}}{0.001}}$$

$$pOH = -\log[OH^{-1}] = -\log[10^{-4}]$$

$pOH = 4$ and $pH = 10$

$$\therefore \quad pH = 14 - pOH = 14 - 4 = 10$$

60 The pK_a of a weak acid, HA is 4.80. The pK_b of a weak base, B OH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be **[AIEEE 2008]**

(a) 9.58 (b) 4.79
(c) 7.01 (d) 9.22

Ans. *(c)*

For salt of weak acid and weak base

$$pH = -\frac{1}{2}[\log K_a + \log K_w - \log K_b]$$

$$= \frac{1}{2}pK_a + \frac{1}{2}pK_w - \frac{1}{2}pK_b$$

$$= \frac{1}{2} \times 4.80 + 7 - \frac{1}{2} \times 4.78$$

$$= 7.01$$

61 The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid ionised is **[AIEEE 2007]**

(a) 4.5 (b) 2.5
(c) 9.5 (d) 7.0

Ans. *(c)*

When HA is 50% ionised, $[HA] = [A^-]$

Buffer solution of weak acid HA → acidic buffer

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

or $pH = pK_a = 4.5$

$pOH = pK_w - pH$

$pOH = 14 - 4.5 = 9.5$

62 Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be **[AIEEE 2005]**

(a) 3.98×10^{-6} (b) 3.68×10^{-6}
(c) 3.88×10^{6} (d) 3.98×10^{8}

Ans. *(a)*

$pH = 5.4$

$$\Rightarrow [H^+] = 10^{-5.4} = 10^{-6} \cdot 10^{0.6}$$

Antilog of 0.6 is ≈ 3.98

$$\therefore \quad [H^+] \approx 3.98 \times 10^{-6}\ M$$

63 Which one of the following statements is not true? **[AIEEE 2003]**

(a) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(b) pH + pOH = 14 for all aqueous solutions
(c) The pH of 1×10^{-8} M HCl is 8
(d) 96,500 C of electricity when passed through a $CuSO_4$ solution deposits 1g equivalent of copper at the cathode

Ans. *(c)*

In 1×10^{-8} M HCl solution, H_2O is also present which also undergoes self ionisation.

$$H_2O \rightleftharpoons H^+ + OH^-$$

10^{-7} M at 25°C[Concentration of water (H_2O)]

If it is taken simply even without common ion effect, higher concentration must be considered which is 10^{-7} M but H^+ from HCl decreases self ionisation of water and hence $[H^+]$ from H_2O.

Hence, net concentration must be smaller than 10^{-7} M.

64 An aqueous solution of 1M NaCl and 1M HCl is **[AIEEE 2002]**

(a) not a buffer but pH < 7
(b) not a buffer but pH > 7
(c) a buffer with pH < 7
(d) a buffer with pH > 7

Ans. *(a)*

NaCl is salt of strong acid and strong base. Its not the case of buffer.

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$NaCl + H_2O \rightleftharpoons NaOH + HCl$

Aqueous NaCl, itself exact neutral solution.

$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

makes solution acidic.

65 On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is **[AIEEE 2004]**

(a) $CH_3COOC_2H_5$ + NaCl

(b) $CH_3COONa + C_2H_5OH$

(c) $CH_3COCl + C_2H_5OH + NaOH$

(d) $CH_3Cl + C_2H_5COONa$

Ans. ***(a)***

Aqueous NaCl is neutral, hence there is no reaction between ethyl acetate and aqueous NaCl.

TOPIC 5
Hydrolsis of Salts

66 Given below are two statements : One is labelled as Assertion (A) and the other labelled as Reason (R).

Assertion (A) During the boiling of water having temporary hardness, $Mg(HCO_3)_2$ is converted to $MgCO_3$.

Reason (R) The solubility product of $Mg(OH)_2$ is greater than that of $MgCO_3$.

In the light of the above statements, choose the most appropriate answer from the options given below

(a) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(b) (A) is true but (R) is false.

(c) Both A and R are true and R is the correct explanation of (A).

(d) (A) is false but (R) is true.

[2021, 18 March Shift-I]

Ans. ***(d)***

During boiling, soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is converted into insoluble $CaCO_3$. This is because of high solubility product of $Mg(OH)_2$ as compared to $MgCO_3$ hence, $Mg(OH)_2$ is precipitated. These precipitates can be removed by filtration. Thus, filtrate will be obtained in soft water.

$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2$

Temporary hardness

$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + CO_2 + 2H_2O$

K_{sp} of $Mg(OH)_2 > K_{sp}$ of $MgCO_3$

and hence, $Mg(OH)_2$ precipitation first.

67 The pH of a 0.02 M NH_4Cl solution will be [Given $K_b(NH_4OH) = 10^{-5}$ and $\log 2 = 0.301$] **[2019, 10 April Shift-II]**

(a) 4.65 (b) 2.65

(c) 5.35 (d) 4.35

Ans. ***(c)***

Key Idea NH_4Cl is a salt of weak base (NH_4OH) and strong acid (HCl). On hydrolysis, NH_4Cl will produce an acidic solution (pH < 7) and the expression of pH of the solution is

$$pH = 7 - \frac{1}{2}(pK_b + \log C)$$

Given, $K_b(NH_4OH) = 10^{-5}$

$\therefore \quad pK_b = -\log K_b = -\log(10^{-5}) = 5$

C = concentration of salt solution = 0.02 M $= 2 \times 10^{-2}$ M

Now, $pH = 7 - \frac{1}{2}(pK_b + \log C)$

On substituting the given values in above equation, we get

$= 7 - \frac{1}{2}[5 + \log(2 \times 10^{-2})]$

$= 7 - \frac{1}{2}[5 + \log 2 - 2]$

$= 7 - \frac{1}{2}[5 + 0.301 - 2]$

$= 7 - 1.65 = 5.35$

68 Which of the following salts is the most basic in aqueous solution? **[JEE Main 2018]**

(a) $Al(CN)_3$

(b) CH_3COOK

(c) $FeCl_3$

(d) $Pb(CH_3COO)_2$

Ans. ***(b)***

Among the given salts

$FeCl_3$ is acidic in nature i.e., have acidic solution as it is the salt of weak base and strong acid.

$Al(CN)_3$ and $Pb(CH_3COO)_2$ are the salts of weak acid and weak base.

CH_3COOK is the salt of strong base and weak acid.

Hence, the solution of CH_3COOK will be most basic because of the following reaction.

$CH_3COOK + H_2O \rightleftharpoons \underset{\text{(Weak acid)}}{CH_3COOH} + \underset{\text{(Strong base)}}{KOH}$

69 pH of 0.005 M calcium acetate (pK_a of $CH_3COOH = 4.74$) is **[AIEEE 2002]**

(a) 7.04 (b) 9.37

(c) 9.26 (d) 8.37

Ans. ***(a)***

Calcium acetate is a salt of weak acid and weak base.

0.005 M calcium acetate, $(CH_3COO)_2Ca$

$\underset{0.005\text{ M}}{(CH_3COO)_2Ca} \rightarrow Ca^{2+} + \underset{(2 \times 0.005 = 0.01)}{2CH_3COO^-}$

$\therefore \quad [CH_3COO^-] = 0.01$ M

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \underset{\text{Alkaline}}{OH^-}$

$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$

$= 7 + 2.37 + \frac{\log 0.01}{2}$

$= 7 + 2.37 - 2.30$

$= 7.04$

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09

Redox Reactions

TOPIC 1
Oxidation, Reduction and Oxidation Number

01 The sum of oxidation states of two silver ions in $[Ag(NH_3)_2][Ag(CN)_2]$ complex is ..... . **[2021, 1 Sep Shift-II]**

Ans. *(2)*

$[Ag(NH_3)_2][Ag(CN)_2]$ complex dissociates into $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$.

Oxidation of Ag in $[Ag(NH_3)_2]^+$

$$Ag + 0 \times 2 = +1$$
$$Ag = +1$$

Oxidation state of Ag in $[Ag(CN)_2]^-$

$$Ag + (-1) \times 2 = -1$$
$$Ag - 2 = -1$$
$$\Rightarrow \quad Ag = +1$$

$\therefore$ Sum of oxidation states of two silver ions in $[Ag(NH_3)_2][Ag(CN)_2]$ complex is 2.

02 Identify the process in which change in the oxidation state is five **[2021, 25 July Shift-II]**

(a) $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

(b) $MnO_4^- \longrightarrow Mn^{2+}$

(c) $CrO_4^{2-} \longrightarrow Cr^{3+}$

(d) $C_2O_4^{2-} \longrightarrow 2CO_2$

Ans. *(b)*

Change in oxidation state in different process is as follows :

(a) $\underset{2x - 14 - 2 = 0}{Cr_2O_7^{2-}} \longrightarrow \underset{x = 6}{2Cr^{3+}}$
$2x = 16$
$x = 8$ ($\therefore 2e^-$ change)

(b) $\underset{x - 8 + 1 = 0}{MnO_4^-} \longrightarrow \underset{x = 2}{Mn^{2+}}$
$x = 7$ ($\therefore 5\,e^-$ change)

(c) $\underset{x - 8 - 2 = 0}{CrO_4^{2-}} \longrightarrow \underset{x = 3}{Cr^{3+}}$
$x = 10$ ($\therefore 7\,e^-$ change)

(d) $\underset{2x - 8 - 2 = 0}{C_2O_4^{2-}} \longrightarrow \underset{x = 4}{2CO_2}$
$x = 5$ ($\therefore 1\,e^-$ change)

Hence, in the process of MnO_4^- to Mn^{2+} the change in oxidation state is five.

03 Cu^{2+} salt reacts with potassium iodide to give **[2021, 20 July Shift-II]**

(a) Cu_2I_2 (b) Cu_2I_3
(c) CuI (d) $Cu(I_3)_2$

Ans. *(a)*

Cu^{2+} salt react with potassium iodide to give Cu_2I_2 (white ppt.)

$$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow \underset{\text{(White ppt.)}}{Cu_2I_2(s)} + I_2$$

In this reaction, Cu^{2+} gets reduced to Cu^+ and I^- gets oxidised to I_2.

04 The species given below that does not show disproportionation reaction is **[2021, 20 July Shift-I]**

(a) BrO_4^- (b) BrO^-
(c) BrO_2^- (d) BrO_3^-

Ans. *(a)*

BrO_4^- will not undergo disproportionation because bromine is in its maximum oxidation state, i.e. + 7.

For a species to undergo disproportionation, the oxidation state of the element undergoing disproportionation should lie between its maximum and minimum possible oxidation values.

In option (a), we have the oxidation state of Br = + 7

In option (b), we have oxidation state of Br = + 1

In option (c), we have oxidation state of Br = + 3

In option (d), we have oxidation state of Br = + 5

The maximum and minimum possible oxidation state value for Br are + 7 and – 1 respectively. So, BrO_4^- cannot oxidise further. Hence, it cannot show disproportionation reaction.

05 In basic medium, H_2O_2 exhibits which of the following reactions ?

A. $Mn^{2+} \rightarrow Mn^{4+}$ B. $I_2 \rightarrow I^-$

C. $PbS \rightarrow PbSO_4$

Choose the most appropriate answer from the options given below. **[2021, 18 March Shift-II]**

(a) A and C (b) Only A
(c) Only B (d) A and B

Ans. *(d)*

In basic medium, oxidising action of H_2O_2

$$Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$$

In basic medium, reducing action of H_2O_2

$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$

In acidic medium, oxidising action of H_2O_2

$$PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$$

Thus, in basic medium H_2O_2 exhibits reaction 'A' and 'B'

Hence, correct option is (d).

06 Given below are two statements.

Statement I Potassium permanganate on heating at 573 K forms potassium manganate.

Statement II Both potassium permanganate and potassium manganate are tetrahedral and paramagnetic in nature.

In the light of the above statements, choose the most appropriate answer from the options given below **[2021, 17 March Shift-I]**

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(a) Statement I is true but statement II is false.
(b) Both statement I and statement II are true.
(c) Statement I is false but statement II is true.
(d) Both statement I and statement II are false.

Ans. ***(a)***

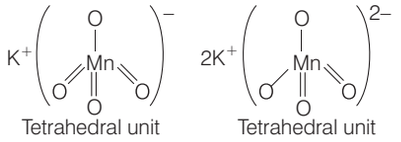
Potassium permanganate on heating at 573 K forms potassium manganate.

$$\overset{+7}{K}MnO_4 \xrightarrow{573\,K} K_2\overset{+6}{Mn}O_4 + MnO_2 + O_2$$

Potassium permanganate (Diamagnetic) — Potassium manganate (Paramagnetic)

Both potassium permanganate and potassium manganate are tetrahedral.

Manganese has four sigma bonds forming tetrahedral structure.



Tetrahedral unit — Tetrahedral unit

$KMnO_4$; $+1+x-8=0$,

$x=+7$

K_2MnO_4; $+2+x-8=0$

$x=+6$

So, Mn is present in + 7 oxidation state in $KMnO_4$ and + 6 oxidation state in K_2MnO_4.

$_{25}Mn=[Ar]4s^2\,3d^5$

$Mn^{+7}=[Ar]4s^0\,3d^0$ (Diamagnetic)

$Mn^{+6}=[Ar]4s^1$ (Paramagnetic)

So, potassium permanganate is diamagnetic and potassium manganate is paramagnetic.

Statement I is true but statement II is false.

07 Dichromate ion is treated with base, the oxidation number of Cr in the product formed is ..... .
[2021, 26 Feb Shift-I]

Ans. ***(6)***

In basic medium dichromate ion ($Cr_2O_7^{2-}$) changes in chromate ion (CrO_4^{2-}).

Oxidation state of Cr in CrO_4^{2-} is +6.

$\Rightarrow$ $CrO_4^{2-}=x+4(-2)=-2$

or $x=+6$.

Dichromate and chromate equilibrium depends on pH of the medium as

$$\underset{(aq)}{\overset{+6}{Cr_2}O_7^{2-}} \underset{H^+\,(pH<7)}{\overset{OH^-\,(pH>7)}{\rightleftharpoons}} \underset{(aq)}{CrO_4^{2-}}$$

(Orange) — (Yellow)

08 Which of the following equation depicts the oxidising nature of H_2O_2?
[2021, 25 Feb Shift-I]

(a) $KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$
(b) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$
(c) $2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$
(d) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$

Ans. ***(c)***

Oxidation involves increase in oxidation number and reduction involves decrease in oxidation number.

$$2I^- + 2H^+ + \overset{1\;-1}{H_2O_2} \longrightarrow \overset{0}{I_2} + \overset{+1\;-2}{2H_2O}$$

In this reaction, H_2O_2 oxidises I^- to I_2 and itself gets reduced to H_2O, so the reaction depicts oxidising nature of H_2O_2. While in other reactions H_2O_2 does not oxidise KIO_4, I_2 and Cl_2.

09 The oxidation states of iron atoms in compounds (*A*), (*B*) and (*C*), respectively, are *x*, *y* and *z*. The sum of *x*, *y* and *z* is

$\underset{(A)}{Na_4[Fe(CN)_5(NOS)]}$,

$\underset{(B)}{Na_4[FeO_4]}$, $\underset{(C)}{[Fe_2(CO)_9]}$

[2020, 9 Sep Shift-I]

Ans. ***(6)***

$Na[\underline{Fe}(CN)_5NOS] \Rightarrow 4\times(+1)+x+5\times(-1)+(+1)+(-2)=0$

$\Rightarrow x=+2$

(CN^-, S^{2-}, NO^+)

$Na_4[\overset{y}{\underline{Fe}}O_4] \Rightarrow 4(+1)+y+4\times(-2)=0$

$\Rightarrow y=+4$

$[\underline{Fe_2}(CO)_9] \Rightarrow 2\times z+9\times 0=0 \Rightarrow z=0$

So, $x+y+z=(+2)+(+4)+(0)=6$

10 The oxidation states of transition metal atoms in $K_2Cr_2O_7$, $KMnO_4$ and K_2FeO_4, respectively, are *x*, *y* and *z*. The sum of *x*, *y* and *z* is ..... .
[2020, 2 Sep Shift-II]

Ans. ***(19)***

$K_2\overset{x}{Cr_2}O_7 \Rightarrow 2(+1)+2x+7\times(-2)=0$

$\Rightarrow$ $x=+6$

$\overset{y}{K}MnO_4 \Rightarrow 1\times(+1)+x+4\times(-2)=0$

$\Rightarrow$ $y=+7$

$K_2\overset{z}{Fe}O_4 \Rightarrow 2\times(+1)+z+4\times(-2)=0$

$\Rightarrow$ $z=+6$

So, $(x+y+z)=6+7+6=19$

11 On heating, lead (II) nitrate gives a brown gas (*A*). The gas (*A*) on cooling changes to a colourless solid/liquid (*B*). (*B*) on heating with NO changes to a blue solid (*C*). The oxidation number of nitrogen in solid (*C*) is
[2020, 4 Sep Shift-I]

(a) + 5 (b) + 4
(c) + 2 (d) + 3

Ans. ***(d)***

On heating lead (II) nitrate following reaction takes place.

$$\underset{\text{(Lead nitrate)}}{Pb(NO_3)_2} \longrightarrow PbO + \underset{\substack{(A)\\ \text{Brown gas}}}{2NO_2} + \frac{1}{2}O_2(g)$$

Gas, NO_2 (*A*) on cooling gives N_2O_4 (*B*).

$$\underset{\text{Brown gas}}{2\,NO_2(g)} \xrightarrow{\text{Cooling}} \underset{(B)}{N_2O_4}$$

Colourless solid/liq. N_2O_4 (*B*) on reaction with NO gives N_2O_3.

$$\underset{(B)}{N_2O_4} + 2NO \xrightarrow{D} \underset{\substack{(C)\\ \text{Blue solid}}}{N_2O_3}$$

Oxidation state of N in N_2O_3 (*C*).

$N_2O_3 \Rightarrow 2x+3(-2)=0$

$2x=+6 \Rightarrow x=\frac{6}{2}=+3$

So, oxidation state is + 3.

12 Oxidation number of potassium in K_2O, K_2O_2 and KO_2, respectively, is
[2020, 7 Jan Shift-I]

(a) +1, +4 and +2 (b) +1, +2 and +4
(c) +1, +1 and +1 (d) +2, +1 and $+\frac{1}{2}$

Ans. ***(c)***

Elements of group 1 (alkali metals) show only one non-zero oxidation number, which is equal to + 1.

K_2O consists of K^+ and O^{2-} ions

K_2O_2 (potassium peroxide) consists of K^+ and O_2^{2-} ions. KO_2 (potassium superoxide) consists of K^+ and O_2^- ions.

Thus, in all the given compounds potassium exhibits +1 oxidation state.

13 The redox reaction among the following is
[2020, 7 Jan Shift-II]

(a) reaction of H_2SO_4 with NaOH
(b) reaction of $[Co(H_2O)_6]Cl_3$ with $AgNO_3$
(c) combination of dinitrogen with dioxygen at 2000 K
(d) formation of ozone from atmospheric oxygen in the presence of sunlight

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Ans. *(c)*

(a) The given reactions are as follows:

$$\underset{(+6)}{H_2SO_4} + 2\underset{(+1)}{NaOH} \longrightarrow \underset{(+1)(+6)}{Na_2SO_4} + 2H_2O$$

(No change in oxidation state, so not a redox reaction).

(b) $[\underset{(+3)}{Co(H_2O)_6}]Cl_3 + 3\ \underset{(+1)}{AgNO_3} \longrightarrow$

$$[\underset{(+3)}{Co(H_2O)_6}](\underset{(+1)}{NO_3})_3 + 3AgCl\downarrow$$

(No change in oxidation state, so not a redox reduction).

(c) $\underset{(0)}{N_2} + \underset{(0)}{O_2} \xrightarrow{200\,K} \underset{(+2)(-2)}{2NO}$

(N_2 oxidised from 0 to +2 oxidation state and O_2 reduced from 0 to –2 oxidation state).

∴ This is redox reaction.

(d) $\underset{(0)}{3O_2} \overset{h\nu}{\rightleftharpoons} \underset{(0)}{2O_3}$

(No change in oxidation states, so not a redox reaction).

14 The compound that cannot act both as oxidising and reducing agent is **[2020, 9 Jan Shift-II]**

(a) H_2SO_3 (b) H_3PO_4
(c) HNO_2 (d) H_2O_2

Ans. *(b)*

In H_3PO_4, P is in its highest oxidation state (+5), it can only act as oxidising agent but not as reducing agents, because it can be reduced but not oxidised.

H_2SO_3 : S = +4 can get oxidised or reduced.

HNO_2 : N = +3 can get oxidised or reduced.

H_2O_2 : O = –1 can get oxidised or reduced.

15 An example of a disproportionation reaction is **[2019, 12 April Shift-I]**

(a) $2MnO_4^- + 10\,I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(b) $2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$

(c) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

(d) $2CuBr \longrightarrow CuBr_2 + Cu$

Ans. *(d)*

In disproportionation reactions, same element undergoes oxidation as well as reduction.

e.g. $\underset{+1}{2CuBr} \longrightarrow \underset{+2}{CuBr_2} + \underset{0}{Cu}$ (Reduction: +1 → 0; Oxidation: +1 → +2)

Here, CuBr get oxidised to $CuBr_2$ and also it get reduced to Cu. Other given reactions and their types are given below.

$$\overset{+7}{2MnO_4^-} + 10\overset{-1}{I^-} + 16H^+ \longrightarrow 2\overset{+2}{Mn^{2+}} + 5\overset{0}{I_2} + 8H_2O$$

(Reduction: +7 → +2; Oxidation: –1 → 0)

In the given reaction, MnO_4^- get oxidised to Mn^{2+} and I^- get reduced to I_2. It is an example of redox reaction. The reaction takes place in acidic medium.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

The given reaction is an example of decomposition reaction. Here, one compound split into two or more simpler compounds, atleast one of which must be in elemental form.

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$$

The given reaction is an example of displacement reaction. In this reaction, an atom (or ion) replaces the ion (or atom) of another element from a compound.

16 Which of the following reactions is an example of a redox reaction? **[JEE Main 2017]**

(a) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

(b) $XeF_2 + PF_5 \longrightarrow [XeF]^+PF_6^-$

(c) $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

(d) $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

Ans. *(a)*

The reaction in which oxidation and reduction occur simultaneously are termed as redox reaction.

$$\overset{+4}{(X)}eF_4 + \overset{+1}{O_2}(F_2) \longrightarrow \overset{+6}{X}eF_6 + \overset{0}{O_2}$$

Since, Xe undergoes oxidation while O undergoes reduction. So, it is an example of redox reaction.

17 In which of the following reactions H_2O_2 acts as a reducing agent? **[JEE Main 2014]**

A. $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$
B. $H_2O_2 - 2e^- \longrightarrow O_2 + 2H^+$
C. $H_2O_2 + 2e^- \longrightarrow 2OH^-$
D. $H_2O_2 + 2OH^- - 2e^- \longrightarrow O_2 + 2H_2O$

(a) A, B (b) C, D
(c) A, C (d) B, D

Ans. *(d)*

The reducing agent oxidises itself by undergoing oxidation through the loss of electrons. Thus, reducing agent reduces other molecules by supplying electrons to them.

(A) $H_2\overset{-1}{O_2} + 2H^+ + 2e^- \longrightarrow 2H_2\overset{-2}{O}$

In this reaction, H_2O_2 undergoes reduction as O shows increase in oxidation number.

(B) $H_2\overset{-1}{O_2} - 2e^- \longrightarrow \overset{0}{O_2} + 2H^+$

In this reaction, H_2O_2 undergoes oxidation as it shows decrease in oxidation number. Thus, H_2O_2 acts as a reducing agent.

(C) $H_2\overset{-1}{O_2} + 2e^- \longrightarrow 2\overset{-2}{O}H^-$

In this reaction, H_2O_2 undergoes reduction.

(D) $H_2\overset{-1}{O_2} + 2OH^- - 2e^- \longrightarrow \overset{0}{O_2} + 2H_2O$

In this reaction, H_2O_2 undergoes reduction. Thus, acts as a reducing agent.

18 The metal that cannot be obtained by the electrolysis of an aqueous solution of its salts is **[JEE Main 2014]**

(a) Ag (b) Ca (c) Cu (d) Cr

Ans. *(b)*

Higher the position of element in the electrochemical series, more difficult is the reduction of its cation. Thus, among all the given elements, only calcium on electrolysis yields H_2 gas at cathode while other yields pure metals at cathode. In case of Ca^{2+} ion, water is reduced in preference to calcium.

For Cr At cathode, $Cr^{3+} + 3e^- \longrightarrow Cr$
For Ag At cathode, $Ag^+ + e^- \longrightarrow Ag$
For Cu At cathode, $Cu^{2+} + 2e^- \longrightarrow Cu$

For Ca^{2+} At cathode,

$$H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-$$

19 Which of the following chemical reactions depicts the oxidising behaviour of H_2SO_4? **[AIEEE 2006]**

(a) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

(b) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$

(c) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

(d) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

Ans. *(a)*

$$\overset{-1}{2HI} + \overset{+6}{H_2SO_4} \longrightarrow \overset{0}{I_2} + \overset{+4}{SO_2} + 2H_2O$$

H_2SO_4 — Reduced to ⟶ SO_2
Oxidising agent

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20 The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is **[AIEEE 2005]**

(a) 0 (b) +1 (c) +2 (d) +3

Ans. ***(d)***

$[Cr(NH_3)_4Cl_2]^+$

Let the oxidation state of Cr = x; $NH_3 = 0$; $Cl = -1$

Net charge = +1

$\therefore$ $[Cr(NH_3)_4Cl_2]^+$

$x + 4\times0 + 2(-1) = +1 \Rightarrow x = 3$

21 The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is **[AIEEE 2005]**

(a) +3 (b) +2

(c) +6 (d) +4

Ans. ***(a)***

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

$Cr_2O_7^{2-}$ is reduced to Cr^{3+}.

Thus, final state of Cr is +3.

22 Among the properties (*A*) reducing, (*B*) oxidising and (*C*) complexing, the set of properties shown by CN^- ion towards metal species is **[AIEEE 2004]**

(a) *A*, *B* (b) *B*, *C*

(c) *C*, *A* (d) *A*, *B*, *C*

Ans. ***(c)***

CN^- is a better complexing agent (*C*) as well as a reducing agent (*A*).

Thus, properties (*A*) and (*C*) are shown

Property (*C*):

$$Ni^{2+} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-}$$

Property (*A*):

$$\underset{\text{II}}{CuCl_2} + 5KCN \longrightarrow \underset{\text{I}}{K_3[Cu(CN)_4]} + \frac{1}{2}(CN)_2 + 2KCl$$

[CN reduces Cu^{2+} to Cu^+]

23 Oxidation number of Cl in $CaOCl_2$ (bleaching powder) is **[AIEEE 2002]**

(a) zero, since it contains Cl_2

(b) −1, since it contains Cl^-

(c) +1, since it contains ClO^-

(d) +1 and −1, since it contains ClO^- and Cl^-

Ans. ***(d)***

$CaOCl_2$ is written basically as Ca(OCl)Cl.

$OCl^- \longrightarrow$ Cl has +1 oxidation state

$Cl^- \longrightarrow$ Cl has −1 oxidation state

24 MnO_4^- is a good oxidising agent in different medium changing to

$$MnO_4^- \longrightarrow Mn^{2+} \longrightarrow MnO_4^{2-} \longrightarrow MnO_2 \longrightarrow Mn_2O_3$$

Changes in oxidation number respectively, are **[AIEEE 2002]**

(a) 1, 3, 4, 5 (b) 5, 4, 3, 2

(c) 5, 1, 3, 4 (d) 2, 6, 4, 3

Ans. ***(c)***

$\overset{+7}{MnO_4^-} \longrightarrow \overset{+2}{Mn^{2+}}$ change 5

$\longrightarrow \overset{+6}{MnO_4^{2-}}$ change 1

$\longrightarrow \overset{+4}{MnO_2}$ change 3

$\longrightarrow \overset{+3}{Mn_2O_3}$ change 4

25 Which of the following is a redox reaction ? **[AIEEE 2002]**

(a) $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$

(b) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$

(c) $Ca(OH)_2 + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$

(d) $2K[Ag(CN)_2] + Zn \longrightarrow 2Ag + K_2[Zn(CN)_4]$

Ans. ***(d)***

(a) $\overset{+1\,-1}{NaCl} + \overset{+1\,-1}{KNO_3} \longrightarrow \overset{+1\,-1}{NaNO_3} + \overset{+1-1}{KCl}$

(b) $\overset{+2}{Ca}\overset{-2}{C_2O_4} + 2\overset{+1-1}{HCl} \longrightarrow \overset{+2\,-1}{CaCl_2} + \overset{+1\,-2}{H_2C_2O_4}$

(c) $\overset{+2\,-1}{Ca(OH)_2} + 2\overset{-3\,+1\,-1}{NH_4Cl} \longrightarrow \overset{+2\,-1}{CaCl_2} + 2\overset{-3\,+1}{NH_3} + 2\overset{+1\,-2}{H_2O}$

In all these cases during reaction, there is no change in oxidation state of ion or molecule or constituent atom. These are simply ionic reactions.

(d) $2K[Ag(CN)_2] + Zn \rightarrow 2Ag + K_2[Zn(CN)_4]$

$Ag^+ \longrightarrow Ag$ gain of e^-, reduction

$Zn \longrightarrow Zn^{2+}$ loss of e^-, oxidation

TOPIC 2
Balancing of Chemical Equations

26 $2MnO_4^- + bC_2O_4^{2-} + cH^+ \longrightarrow x\,Mn^{2+} + y\,CO_2 + zH_2O$

If the above equation is balanced with integer coefficients, the value of c is ..... .

[2021, 16 March Shift-I]

Ans. ***(16)***

Balancing by half-reaction method

$$\overset{+7}{2MnO_4^-} + b\overset{+3}{C_2O_4^{2-}} + cH^+ \longrightarrow x\overset{+2}{Mn^{+2}} + y\overset{+4}{CO_2} + zH_2O$$

Step 1 Separate two half-reactions

Oxidation half (O.H.) $C_2O_4^{2-} \longrightarrow CO_2$

Reduction half (R.H.) $MnO_4^- \longrightarrow Mn^{2+}$

Step 2 Balance all the atoms except oxygen and 'H'.

O.H. $C_2O_4^{2-} \longrightarrow 2CO_2$

R.H. $MnO_4^- \longrightarrow Mn^{2+}$

Step 3 Balance 'O' by adding H_2O and 'H' by adding H^+.

O.H. $C_2O_4^{2-} \longrightarrow 2CO_2$

R.H. $8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

Step 4 Balance charge by adding electron

O.H $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

R.H. $5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

Step 5 Balance electron by multiplying O.H. by '5' and R.H. by '2'.

O.H. $5C_2O_4^{2-} \longrightarrow 10\,CO_2 + 10e^-$

R.H. $10e^- + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 8H_2O$

Step 6 Add both half-reaction

$16H^+ + 5C_2O_4^{2-} + 2MnO_4^- \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

So, $c = 16$

27 In basic medium CrO_4^{2-} oxidises $S_2O_3^{2-}$ to form SO_4^{2-} and itself changes into $Cr(OH)_4^-$. The volume of 0.154 M CrO_4^{2-} required to react with 40 mL of 0.25 M $S_2O_3^{2-}$ is ..... mL

(Rounded off to the nearest integer). **[2021, 25 Feb Shift-I]**

Ans. ***(173)***

Given, Molarity of CrO_4^{2-} (M_1) = 0.154 M

Molarity of $S_2O_3^{2-}$ (M_2) = 0.25M

Volume of $S_2O_3^{2-}$ (V_2) = 40 mL

Volume of CrO_4^{2-} (V_1) = ?

$$\overset{+6\ 2-}{CrO_4} + \overset{+6\ 2-}{S_2O_3} \longrightarrow \overset{+6}{SO_4^{2-}} + \overset{+3}{Cr(OH)_4^-}$$

Gram equivalent of CrO_4^{2-} = Gram equivalent of $S_2O_3^{2-}$

$N_1V_1 = N_2V_2$

Normality = Molarity × n factor

n for Cr = 6 − 3 = 3

n for S $\Rightarrow S_2O_3^{2-} \longrightarrow 2\,SO_4^{2-} + 8e^-$

$0.154 \times 3 \times V_1 = 0.25 \times 40 \times 8$

$V_1 = 173$ mL

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28 The reaction of sulphur in alkaline medium is given below

$S_8(s) + aOH^-(aq) \longrightarrow bS^{2-}(aq) + cS_2O_3^{2-}(aq) + dH_2O(l)$

The value of '*a*' is ..... . (Integer answer) **[2021, 24 Feb Shift-I]**

Ans. ***(12)***

The two half reaction, one separately are as follows

$$S_8 + 16e^- \longrightarrow 8S^{2-} \quad \text{(Reduction)}$$

$$S_8 + 12H_2O \longrightarrow 4S_2O_3^{2-} + 24H^+ + 16e^- \quad \text{(Oxidation)}$$

$$2S_8 + 12H_2O \longrightarrow 8S^{2-} + 4S_2O_3^{2-} + 24H^+$$

For balancing in basic medium,

Add an equal number of OH^- that of H^+, we get

$$2S_8 + 12H_2O + 24OH^- \longrightarrow 8S^{2-} + 4S_2O_3^{2-} + 24H_2O$$

$$2S_8 + 24OH^- \longrightarrow 8S^{2-} + 4S_2O_3^{2-} + 12H_2O$$

or $S_8 + 12OH^- \longrightarrow 4S^{2-} + 2S_2O_3^{2-} + 6H_2O$ ...(i)

On comparing (i) with

$S_8 + aOH^-(aq) \longrightarrow bS^{2-}(aq) + cS_2O_3^{2-} + dH_2O$

We get, $a = 12; b = 4; \quad c = 2; \quad d = 6$

29 Consider the following equations :

$2Fe^{2+} + H_2O_2 \longrightarrow xA + yB$ (in basic medium)

$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow x'C + y'D + z'E$ (in acidic medium)

The sum of the stoichiometric coefficients x, y, x', y' and z' for products *A*, *B*, *C*, *D* and *E*, respectively, is ..... . **[2020, 4 Sep Shift-II]**

Ans. ***(19)***

In basic medium

$$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 2$$

$$H_2O_2 + 2e^- \longrightarrow 2HO^-$$

$$2Fe^{2+} + H_2O_2 \longrightarrow \underset{(A)}{2Fe^{3+}} + \underset{(B)}{2HO^-}$$

Hence, $x = 2$ and $y = 2$.

In acidic medium

$$[8H^+ + MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$[H_2O_2 \longrightarrow O_2(g) + 2H^+ + 2e^-] \times 5$$

$$16H^+ + 2MnO_4^- + 5H_2O_2 \longrightarrow \underset{(C)}{2Mn^{2+}} + \underset{(D)}{8H_2O} + \underset{(E)}{5O_2(g)}$$

So, $x' = 2, y' = 8, z' = 5$

So, $x + y + x' + y' + z'$

$\Rightarrow 2 + 2 + 2 + 8 + 5 \Rightarrow 19$

30 In order to oxidise a mixture of one mole of each of FeC_2O_4, $Fe_2(C_2O_4)_3$, $FeSO_4$ and $Fe_2(SO_4)_3$ in acidic medium, the number of moles of $KMnO_4$ required is **[2019, 8 April Shift-I]**

(a) 2 (b) 1 (c) 3 (d) 1.5

Ans. ***(a)***

The oxidation of a mixture of one mole of each of FeC_2O_4, $Fe_2(C_2O_4)_3$ $FeSO_4$ and $Fe_2(SO_4)_3$ in acidic medium with $KMnO_4$ is as follows

$FeC_2O_4 + KMnO_4 \longrightarrow Fe^{3+} + CO_2 + Mn^{2+}$ ...(i)

$Fe_2(C_2O_4)_3 + KMnO_4 \longrightarrow Fe^{3+} + CO_2 + Mn^{2+}$ ...(ii)

$FeSO_4 + KMnO_4 \longrightarrow Fe^{3+} + SO_4^{2-} + Mn^{2+}$ ...(iii)

Change in oxidation number of Mn is 5.

Change in oxidation number of Fe in (i), (ii) and (iii) are +3, + 6, + 1, respectively.

$n_{eq}KMnO_4 = n_{eq}[FeC_2O_4 + Fe_2(C_2O_4)_3 + FeSO_4]$

$n \times 5 = 1 \times 3 + 1 \times 6 + 1 \times 1 \Rightarrow n = 2$

31 In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is

(a) 2 (b) 5 (c) 1 (d) 10 **[2019, 10 Jan Shift-II]**

Ans. ***(c)***

Reaction of oxalate with permanganate in acidic medium.

$$5C_2O_4^{2-} + 2MnO_4^- \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

n-factor : $(4-3)\times 2 = 2 \quad (7-2) = 5$

No. of mole	5	2	10

$\Rightarrow 5C_2O_4^{2-}$ ions transfer 10 e^- to produce 10 molecules of CO_2. So, number of electrons involved in producing 10 molecules of CO_2 is 10.

Thus, number of electrons involved in producing 1 molecule of CO_2 is 1.

32 Consider the following reaction,

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \longrightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$

The values of *x*, *y* and *z* in the reaction are, respectively **[AIEEE 2013]**

(a) 5, 2 and 16
(b) 2, 5 and 8
(c) 2, 5 and 16
(d) 5, 2 and 8

Ans. ***(c)***

The half equations of the reaction are

$$MnO_4^- \longrightarrow Mn^{2+}$$

$$C_2O_4^{2-} \longrightarrow CO_2$$

The balanced half equations are

$$(MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O) \times 2$$

$$(C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-) \times 5$$

Equating number of electrons, we get

$$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$$

$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$$

On adding both the equations, we get

$$2MnO_4^- + 5C_2O_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 2 \times 5CO_2 + \frac{16}{2}H_2O$$

Thus, *x*, *y* and *z* are 2, 5 and 16, respectively.

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10
Electrochemistry

TOPIC 1
Electrolytic Conductance Electrolysis and its Quantitative Aspect

01 If the conductivity of mercury at 0°C is 1.07×10^{6} S m^{-1} and the resistance of a cell containing mercury is 0.243 Ω, then the cell constant of the cell is $x\times10^{4}$ m^{-1}. The value of x is ..... . (Nearest integer) **[2021, 1 Sep Shift-II]**

Ans. ***(26)***

Conductance (G) is reciprocal of resistance (R).

$$R=\frac{1}{G} \text{ or } G=\frac{1}{R}=\frac{1}{0.243\,\Omega}$$

$$=4.115\,\Omega^{-1}$$

Relation between conductance (G), conductivity (κ) and cell constant $\left(\frac{l}{A}\right)$ is given as

$$\kappa=\frac{Gl}{A}$$

$$\Rightarrow \quad \frac{l}{A}=\frac{\kappa}{G}=\frac{1.07\times10^{6}\ \text{S m}^{-1}}{4.115\,\Omega^{-1}}$$

$$=26\times10^{4}\ \text{m}^{-1} \Rightarrow x=26$$

$\therefore$ Answer is 26.

02 Match List-I with List-II.

	List-I (Parameter)		List-II (Unit)
A.	Cell constant	1.	S cm^2 mol^{-1}
B.	Molar conductivity	2.	Dimensionless
C.	Conductivity	3.	m^{-1}
D.	Degree of dissociation of electrolyte	4.	Ω^{-1}m^{-1}

Choose the most appropriate answer from the options given below **[2021, 31 Aug Shift-II]**

	A	B	C	D		A	B	C	D
(a)	3	1	4	2	(b)	3	1	2	4
(c)	1	4	3	2	(d)	2	1	3	4

Ans. ***(a)***

(A) Cell constant $=\frac{l}{A}\text{m}^{-1}$

(B) Molar conductivity

$$(\lambda_m)=\frac{\kappa\times1000}{\text{molarity}}\text{Scm}^2\ \text{mol}^{-1}$$

(C) Conductivity $(\kappa)=\frac{1}{\rho}=\frac{1}{RA}\Omega^{-1}\text{m}^{-1}$

(D) Degree of dissociation of electrolyte = Number of moles dissociated out of one mole.

It is a ratio. Hence, it is dimensionless.

Thus, the correct match is

A $\rightarrow$ 3, B $\rightarrow$ 1, C $\rightarrow$ 4, D $\rightarrow$ 2.

03 The resistance of a conductivity cell with cell constant 1.14 cm^{-1}, containing 0.001 M KCl at 298 K is 1500 Ω. The molar conductivity of 0.001 M KCl solution at 298 K in S cm^{2}mol^{-1} is ..... . (Integer answer) **[2021, 27 Aug Shift-II]**

Ans. ***(760)***

Given, $G^*=1.14\ \text{cm}^{-1}=1.14\times10^{3}\ \text{m}^{-1}$

$R=1500\,\Omega$

$C=0.001$ M

$G^*=R\times\kappa$

[where, R = resistance

G^* = cell constant

κ = conductivity

C = concentration]

$$\therefore \quad \kappa=\frac{G^*}{R}=\frac{1.14\times10^{3}\ \text{m}^{-1}}{1500}$$

$$\Lambda_m=\frac{\kappa}{C}$$

[where, Λ_m = molar conductivity]

$$=\frac{1.14\times10^{3}}{1500\times0.001}=760\ \text{S cm}^2\ \text{mol}^{-1}.$$

04 The conductivity of a weak acid HA of concentration 0.001 mol L^{-1} is 2.0×10^{-5} S cm^{-1}. If $\Lambda^{\circ}_m(HA)=190$ S cm^2 mol^{-1}, the ionisation constant (K_a) of HA is equal to ..... $\times10^{-6}$. (Round off to the nearest integer) **[2021, 27 July Shift-I]**

Ans. ***(12)***

Using formula for molar conductivity.

$$\Lambda_m=1000\times\frac{\text{Conductivity}\,(\kappa)}{\text{Concentration}\,(M)}$$

$$=1000\times\frac{2\times10^{-5}}{0.001}$$

$$=20\ \text{S cm}^2\ \text{mol}^{-1}$$

$\Rightarrow$ Degree of dissociation,

$$\alpha=\frac{\Lambda_m}{\Lambda^{\infty}_m}=\frac{20}{190}=\frac{2}{19}$$

where (use the symbol and meaning marked)

$$\underset{0.001(1-\alpha)}{HA} \rightleftharpoons \underset{0.001\,\alpha}{H^+} + \underset{0.001\,\alpha}{A^-}$$

$$\Rightarrow \quad K_a=0.001\left(\frac{\alpha^2}{1-\alpha}\right)$$

$$=\frac{0.001\times\left(\frac{2}{19}\right)^2}{1-\left(\frac{2}{19}\right)}=12.3\times10^{-6}$$

05 Given below are two statements.

Statement I The limiting molar conductivity of KCl (strong electrolyte) is higher compared to that of CH_3COOH (weak electrolyte).

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Statement II Molar conductivity decreases with decrease in concentration of electrolyte.

In the light of the above statements, choose the most appropriate answer from the options given below

[2021, 26 Aug Shift-I]

(a) Statement I is true but statement II is false.
(b) Statement I is false but statement II is true.
(c) Both statement I and statement II are true.
(d) Both statement I and statement II are false.

Ans. ***(d)***

Limiting molar conductivity of KCl

$\Lambda_m^\circ KCl = \Lambda_m^\infty(K^+) + \Lambda_m^\infty(Cl^-)$

$= 73.55\ S\ cm^2/mol + 76.3\ S\ cm^2/mol$

$= 149.3\ S\ cm^2/mol$

Limiting molar conductivity of CH_3COOH

$\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\infty(CH_3COO^-) + \Lambda_m^\infty(H^+)$

$= 349.8\ S\ cm^2/mol + 40.9\ S\ cm^2/mol$

$= 390.7\ S\ cm^2/mol$

$\therefore$ Limiting molar conductivity of CH_3COOH is more than KCl. Hence, statement I is false.

Also, as the concentration decreases, dilution of the electrolyte increases which will increase the degree of dissociation of weak electrolyte. Thus, the number of ions in the solution increases and hence, the molar conductance of electrolyte increases. Therefore, we can see that with decrease in concentration of electrolyte, molar conductance increases.

Hence, statement II is also false.

06 Potassium chlorate is prepared by electrolysis of KCl in basic solution as shown by following equation

$6OH^- + Cl^- \longrightarrow ClO_3^- + 3H_2O + 6e^-$

A current of xA has to be passed for 10th to produce 10.0 g of potassium chlorate. The value of x is ..... . (Nearest integer)

(Molar mass of $KClO_3 = 122.6\ g\ mol^{-1}$, $F = 96500\ C$)

[2021, 20 July Shift-II]

Ans. ***(1)***

Given, balanced equation is

$6OH^- + Cl^- \longrightarrow ClO_3^- + 3H_2O + 6e^-$

$W = Q \times I \times t$

$$W = \frac{E}{F} \times I \times t \qquad \left(\because Q = \frac{E}{F}\right)$$

where, W = weight of potassium chlorate

E = Molar mass of potassium chlorate

F = Faraday's constant

I = Current

t = Time for which current is passed

$$10 = \frac{122.6}{96500 \times 6} \times x \times\ 10 \times 3600$$

$$x = \frac{96500 \times 6 \times 10}{10 \times 3600 \times 122.6}$$

$\Rightarrow \quad x = 1.311$

07 A KCl solution of conductivity $0.14\ S\ m^{-1}$ shows a resistance of $4.19\ \Omega$ in a conductivity cell. If the same cell is filled with an HCl solution, the resistance drops to $1.03\ \Omega$. The conductivity of the HCl solution is ..... $\times 10^{-2}\ S\ m^{-1}$ (Round off to the nearest integer)

[2021, 17 March Shift-II]

Ans. ***(57)***

Given,

Conductivity of KCl solution $k_{KCl} = 0.14\ Sm^{-1}$

$R_{KCl} = 4.19$ ohm

$R_{HCl} = 1.03$ ohm

To find conductivity of HCl solution k_{HCl}

We know that,

$k = 1/R \cdot G^*$

where k is the conductivity, R is the resistance and G^* is the cell constant.

As k is constant. Therefore, k and G^* constant

$\therefore \quad k_{KCl} \cdot R_{KCl} = k_{HCl} \cdot R_{HCl}$

Therefore, $0.14 \times 4.19 = k \times 1.03$

or, k of HCl solution $= \dfrac{0.14 \times 4.19}{1.03}$

$= 0.5695\ Sm^{-1} = 56.95 \times 10^{-2}\ Sm^{-1}$

$= 57 \times 10^{-2}\ Sm^{-1}$

08 A 5.0 m mol dm^{-3} aqueous solution of KCl has a conductance of 0.55 mS when measured in a cell constant $1.3\ cm^{-1}$.

The molar conductivity of this solution is ..... $mSm^2\ mol^{-1}$.

(Round off to the nearest integer)

[2021, 16 March Shift-II]

Ans. ***(14)***

Given, concentration of KCl

$(C) = 5$ m mol / L

$= 5 \times 10^{-3}$ mol/L

Conductance (G) = 0.55 mS

Cell constant $\dfrac{l}{A} = 1.3\ cm^{-1}$

$$\Lambda_m = \frac{\kappa}{1000 \times C}$$

where, Λ_m = molar conductivity

κ = conductivity, C = molarity

Conductivity $(\kappa) = G\dfrac{l}{A}$

$= 0.55 \times (1.3 \times 100)$

$= 55 \times 1.3$

$$\Lambda_m = \frac{55 \times 1.3}{1000 \times 5 \times 10^{-3}}$$

$\Lambda_m = 14.3$

Closest integer,

$\Lambda_m = 14$

09 Consider the following reaction,

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O,\ E^\circ = 1.51$ V.

The quantity of electricity required in Faraday to reduce five moles of MnO_4^- is ..... .

[2021, 26 Feb Shift-I]

Ans. ***(25)***

In the reduction half-cell,

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

1 mol 5F

5 mol 25 F

As one mole of MnO_4^- required 5F of charge,

5 moles of MnO_4^- will require charge,

$Q = 5 \times 5$ Faraday $= 25$ Faraday

10 Amongst the following, the form of water with the lowest ionic conductance at 298 K is

[2020, 9 Jan Shift-II]

(a) saline water used for intravenous injection
(b) distilled water
(c) water from a well
(d) sea water

Ans. ***(b)***

Among the given options, distilled water has the lowest ionic conductance at 298 K.

Water from well or sea contains mineral ions,

$\therefore$ they have ionic conductance.

Saline water is an electrolyte and contain ions.

$\therefore$ It also has ionic conductance.

11 Let C_{NaCl} and C_{BaSO_4} be the conductances (in S) measured for saturated aqueous solutions of

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$NaCl$ and $BaSO_4$, respectively, at a temperature T. Which of the following is false? **[2020, 3 Sep Shift-I]**

(a) Ionic mobilities of ions from both salts increase with T.
(b) $C_{BaSO_4}(T_2) > C_{BaSO_4}(T_1)$ for $T_2 > T_1$
(c) $C_{NaCl}(T_2) > C_{NaCl}(T_1)$ for $T_2 > T_1$
(d) $C_{NaCl} >> C_{BaSO_4}$ at a given T

Ans. ***(c)***

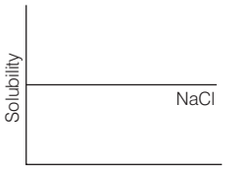
$NaCl$ is a strong electrolyte, whereas $BaSO_4$ is a sparingly soluble (weaker) electrolyte. So, even in saturated solution, $NaCl$ will almost remain in dissociated form to give free Na^+ and Cl^-. But availibility of Ba^{2+} and SO_4^{2-} in water will be very poor.

But degree of dissociation of $BaSO_4$ will increase with a temperature to give more ions.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2+}(aq)$$

Again, with increase in temperature ionic mobility also increases. So, options (a), (b) and (d) are true but (c) is false.

Solubility of $NaCl$ in water remains almost constant with increase in temperature. So, option (c) is false.



12 An acidic solution of dichromate is electrolysed for 8 minutes using 2A current. As per the following equation

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

The amount of Cr^{3+} obtained was 0.104 g. The efficiency of the process(in %) is
(Take : $F = 96000$ C, atomic mass of chromium = 52) ..... .
[2020, 3 Sep Shift-II]

Ans. ***(60)***

Given,

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$\text{Number of moles} = \left(\frac{8 \times 60 \times 2}{96000}\right) \quad [\because F = 96000\ \text{C}]$$

Using stoichiometry,

$$\frac{n_e \text{ (used)}}{6} = \frac{n_{Cr^{3+}} \text{ (Produced)}}{2}$$

$$\Rightarrow n_{Cr^{3+}} \text{ produced} = \frac{2}{6} \times \frac{8 \times 60 \times 2}{96000} = \frac{1}{30}$$

Theoritically produced

$$\text{Weight}_{Cr^{3+}} = \left(\frac{1}{30} \times 52\right) \text{g} \quad [\because \text{Mass of Cr} = 52]$$

Weight actual = 0.104 g

$$\text{Efficiency} = \frac{\text{Weight}_{(\text{actual})}}{\text{Weight}_{(\text{theoritical})}} \times 100$$

Efficiency of the process

$$= \frac{0.104\ \text{g}}{\left(\frac{1}{30} \times 52\right)} \times 100 = 60\%$$

13 250 mL of a waste solution obtained from the workshop of a goldsmith contains 0.1 M $AgNO_3$ and 0.1 M $AuCl$. The solution was electrolysed at 2 V by passing a current of 1 A for 15 minutes. The metal /metals electrodeposited will be ($E^\circ_{Ag^+/Ag} = 0.80$ V, $E^\circ_{Au^+/Au} = 1.69$ V) **[2020, 4 Sep Shift-II]**

(a) only silver
(b) silver and gold in equal mass proportion
(c) only gold
(d) silver and gold in proportion to their atomic weights

Ans. ***(c)***

$$\text{Charge}(q) = \frac{it}{96500} \text{F}$$

$$= \frac{1 \times 15 \times 60}{96500} = \frac{900}{96500} = \frac{9}{965} \text{F} = 0.0093\ \text{F}$$

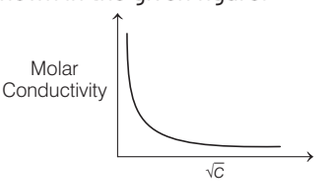
Number of moles of $Au^+ = 0.01$ and number of moles of $Ag^+ = 0.01$

Species with higher value of standard reduction potential, ($E^\circ_{Au^+/Au} = 1.69$ V) will get deposited first at cathode.

$$\underset{0.01}{Au^+(aq)} + e^- \rightarrow \underset{0.0093\ \text{mol}}{Au(s)}$$

So, only Au will get deposited.

14 The variation of molar conductivity with concentration of an electrolyte (X) in aqueous solution is shown in the given figure.



The electrolyte X is
[2020, 5 Sep Shift-II]

(a) HCl (b) NaCl
(c) KNO_3 (d) CH_3COOH

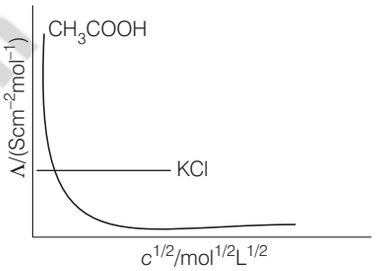
Ans. ***(d)***

Molar and activity, λ_m is defined as the conducting power of all the ion produced by dissolving one gram mole of on electrolyte in solution. it is a function of the ionic strength of a solution.

The molar conductivity of both weak and strong electrolytes increases with decrease in concentration.

Molar conductivity is the conductivity affered by one mole of ions.

Increased dilution results in the dissociation of more electrolytes into ions and effectively increasing the number of active ions in the solution. These active ions impart more conductivity.



15 Potassium chlorate is prepared by the electrolysis of KCl in basic solution
$6OH^- + Cl^- \rightarrow ClO_3^- + 3H_2O + 6e^-$. If only 60% of the current is utilised in the reaction, the time (rounded to the nearest hour) required to produce 10 g of $KClO_3$ using a current of 2 A is ..... .
(Given : $F = 96{,}500$ C mol^{-1}; molar mass of $KClO_3 = 122$ g mol^{-1})
[2020, 6 Sep Shift-I]

Ans. ***(11.00)***

For 1 mole of ClO_3^-, 6 F charge required but current efficiency is only 60%. So, to obtain 1 mol ClO_3^-, charged required is 10 F.

$$\text{Now, moles of } KClO_3 = \frac{10\ \text{g}}{122}$$

$$\therefore \quad \text{Charge} = \frac{10}{122} \times 10\ \text{F}$$

$\therefore$ Current using = 2 A

Apply, $W = Z \times I \times t$

$$\therefore \quad \frac{100}{122} = \frac{2}{96500} \times 2 \times 3600$$

$$\Rightarrow \quad t = 11\ \text{hrs}$$

Hence, the correct answer is (11).

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16 The equation that is incorrect is
[2020, 7 Jan Shift-II]

(a) $(\Lambda^\circ_m)_{NaBr} - (\Lambda^\circ_m)_{NaCl} = (\Lambda^\circ_m)_{KBr} - (\Lambda^\circ_m)_{KCl}$

(b) $(\Lambda^\circ_m)_{KCl} - (\Lambda^\circ_m)_{NaCl} = (\Lambda^\circ_m)_{KBr} - (\Lambda^\circ_m)_{NaBr}$

(c) $(\Lambda^\circ_m)_{NaBr} - (\Lambda^\circ_m)_{NaI} = (\Lambda^\circ_m)_{KBr} - (\Lambda^\circ_m)_{NaBr}$

(d) $(\Lambda^\circ_m)_{H_2O} = (\Lambda^\circ_m)_{HCl} + (\Lambda^\circ_m)_{NaOH} - (\Lambda^\circ_m)_{NaCl}$

Ans. ***(c)***

According to Kohlrausch's law,

Limiting molar conductivity of an electrolyte is the sum of the individual contributions of the cation and the anion of the electrolyte. Therefore,

for option (a).

$\lambda^\circ_m(Na^+) + \lambda^\circ_m(Br^-) - \lambda^\circ_m(Na^+) - \lambda^\circ_m(Cl^-)$
$= \lambda^\circ_m(K^+) + \lambda^\circ_m(Br^-) - \lambda^\circ_m(K^+) - \lambda^\circ_m(Cl^-)$
or $\lambda^\circ_m(Br^-) - \lambda^\circ_m(Cl^-) = \lambda^\circ_m(Br^-) - \lambda^\circ_m(Cl^-)$

$\therefore$ LHS = RHS

$\therefore$ The LHS of option (a)
$= \lambda^\circ_m(Br^-) - \lambda^\circ_m(Cl^-)$
and also RHS of that
$= \lambda^\circ_m(Br^-) - \lambda I^\circ_m(Cl^-)$
LHS = RHS

For option (b),

$\lambda^\circ_m(K^+) + \lambda^\circ_m(Cl^-) - \lambda^\circ_m(Na^+) - \lambda^\circ_m(Cl^-)$
$= \lambda^\circ_m(K^+) + \lambda^\circ_m(Br^-) - \lambda^\circ_m(Na^+) - \lambda^\circ_m(Br^-)$
or $\lambda^\circ_m(K^+) - \lambda^\circ_m(Na^+) = \lambda^\circ_m(K^+) - \lambda^\circ_m(Na^+)$

$\therefore$ LHS = RHS

Similarly for option (c),
$LHS = \lambda^\circ_m(Br^-) - \lambda^\circ_m(I^-)$
and $RHS = \lambda^\circ_m(K^+) - \lambda^\circ_m(Na^+)$
$\therefore$ LHS $\neq$ RHS

And for option (d), also
$\lambda^\circ_m(H^+) + \lambda^\circ_m(OH^-) = \lambda^\circ_m(H^+) + \lambda^\circ_m(OH^-)$

$\therefore$ LHS = RHS

Thus, the correct answer is (c).

17 108 g of silver (molar mass 108 g mol^{-1}) is deposited at cathode from $AgNO_3(aq)$ solution by a certain quantity of electricity. The volume (in L) of oxygen gas produced at 273 K and 1 bar pressure from water by the same quantity of electricity is .....
[2020, 9 Jan Shift-II]

Ans. ***(5.66)***

Equal quantity of electricity produces same number of equivalents of products in electrolysis.

$\therefore$ No. of equivalent of O_2 produced = No. of equivalents of Ag produced

No. of equivalent of Ag
$= \frac{\text{Mass}}{\text{Equivalent mass}} = \frac{108}{108} = 1.$

$\therefore$ No. of equivalents of O_2 formed = 1.

For production of O_2 from water

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

n-factor = 4

$\therefore 1 \text{ equivalent} = \frac{1}{4} \text{ moles}$

Volume of gas at 273 K and 1 bar pressure
$= 22.7 \times n = 22.7 \times \frac{1}{4} = 5.675 \text{ L}$

18 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode?
[2019, 9 April Shift-II]

(a) 0.20 (b) 0.10
(c) 0.15 (d) 0.05

Ans. ***(d)***

A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. It means that 0.1 equivalent of Ni^{2+} will be discharged.

Electrolysis of $Ni(NO_3)_2$ gives

$Ni^{2+} + 2e^- \longrightarrow Ni$
(Atomic mass of Ni = 58.7)

Number of equivalents = Number of moles × number of electrons.

0.1 = Number of moles × 2

$\therefore$ Number of moles of $Ni = \frac{0.1}{2} = 0.05$

19 Consider the statements S_1 and S_2 :

S_1 : Conductivity always increases with decrease in the concentration of electrolyte.

S_2 : Molar conductivity always increases with decrease in the concentration of electrolyte.

The correct option among the following is **[2019, 10 April Shift-I]**

(a) S_1 is correct and S_2 is wrong
(b) S_1 is wrong and S_2 is correct
(c) Both S_1 and S_2 are wrong
(d) Both S_1 and S_2 are correct

Ans. ***(b)***

The explanation of statements (S_1 and S_2) are as follows :

In conductivity cell, conductivity (κ) is equal to the sum of ionic conductances (c), of an electrolytic solution present is unit volume of the solution enclosed by two electrodes of unit area ($a \neq 1$) separated by a unit length ($l = 1$).

$\kappa = c \times \frac{l}{a}$

$\Rightarrow \kappa = c$ when $l = 1, a = 1$

So, with decrease in the concentration of electrolyte, number of ions in the given unit volume also decreases, i.e. κ [conductivity] also decreases.

Thus, statement S_1 is wrong. S_2 : Molar conductivity (λ_m) is defined as the conducting power of all the ions present in a solution containing 1 mole of an electrolyte.

$\lambda_m = \kappa \times V_{mL}$
$= \kappa \times \frac{1000}{M}$

where, V_{mL} = volume in mL containing 1 mole of electrolyte

m = molar concentration (mol/L)

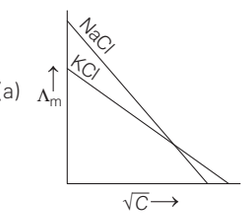
So, in a conductivity cell

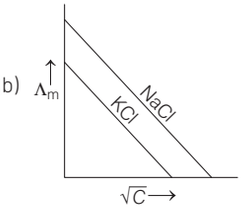
$\lambda_m \propto \frac{1}{M}$

i.e. molar conductivity increases with decrease in the concentration (M) of electrolyte.

Thus, statement S_2 is correct.

20 Which one of the following graphs between molar conductivity (Λ_m) *versus* $\sqrt{C}$ is correct?
[2019, 10 April Shift-II]

(a) 

(b) 

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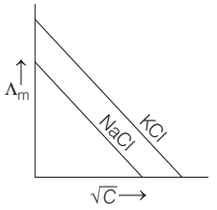
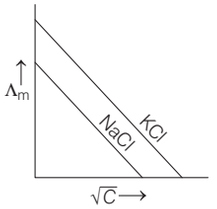
(c) 

(d) 

Ans. ***(c)***

NaCl and KCl are strong electrolytes. So, the study of their molar conductances (λ_m) can be experimentally verified by Debye-Huckel Onsagar equation,

$$\Lambda_m^c = \Lambda_m^\infty - B\sqrt{C}$$

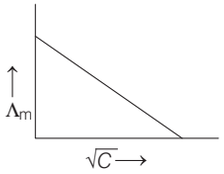
Λ_m^c = molar conductance at concentration.

Λ_m^∞ = molar conductance at infinite dilution.

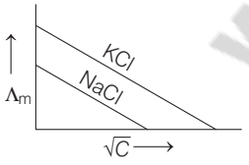
i.e. $C \to 0$

B = Debye-Huckel Onsagar constant.

For (both NaCl and KCl) a strong binary electrolyte like AB, the nature of the plot of Λ_m *vs* $\sqrt{C}$ will be



Size of $Na^{\oplus}$ is being smaller than $K^{\oplus}$ and $Na^{\oplus}$ will remain in more hydrated state, i.e. larger sized in aqueous solution. As a result, ionic mobility as well as ionic conductance of $Na^{\oplus}$ (or NaCl as $Cl^{\ominus}$ is common to NaCl and KCl) will be lower than $K^{\oplus}$ (or KCl). Thus, the plot of Λ_m *vs* $\sqrt{C}$ for NaCl and KCl is as follows :



21 Λ°_m for NaCl, HCl and Na*A* are 126.4, 425.9 and 100.5 S cm^2 mol^{-1}, respectively. If the conductivity of 0.001 M H*A* is 5×10^{-5} S cm^{-1}, degree of dissociation of H*A* is

[2019, 12 Jan Shift-II]

(a) 0.25 (b) 0.50 (c) 0.75 (d) 0.125

Ans. ***(d)***

According to Kohlrausch's law, the molar conductivity of H*A* at infinite dilution is given as,

$$\Lambda^\circ_m(HA) = [\Lambda^\circ_m(H^+) + \Lambda^\circ_m(Cl^-)] + [\Lambda^\circ_m(Na^+) + \Lambda^\circ_m(A^-)] - [\Lambda^\circ_m(Na^+) + \Lambda^\circ_m(Cl^-)]$$

$$= 425.9 + 100.5 - 126.4$$

$$= 400 \text{ S cm}^2 \text{ mol}^{-1}$$

Also, molar conductivity at given concentration is given as,

$$\Lambda_m = \frac{1000\times\kappa}{M}$$

Given, κ = conductivity $\Rightarrow 5\times10^{-5}$ S cm^{-1}

M = Molarity $\Rightarrow$ 0.001 M

$$\therefore \quad \Lambda_m = \frac{1000\times5\times10^{-5}\text{ S cm}^{-1}}{10^{-3}\text{ M}}$$

$$= 50 \text{ S cm}^2 \text{ mol}^{-1}$$

Therefore, degree of dissociation (α), of H*A* is,

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{50 \text{ S cm}^2\text{mol}^{-1}}{400 \text{ S cm}^2\text{mol}^{-1}} = 0.125$$

22 How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane?
(Atomic weight of $B = 10.8\,\mu$)

[JEE Main 2018]

(a) 6.4 hours (b) 0.8 hours
(c) 3.2 hours (d) 1.6 hours

Ans. ***(c)***

Given that, i = 100 amp. also, 27.66 g of diborane (B_2H_6)

Molecular mass of B_2H_6

$$= 10.8\times2 + 6 = 27.6$$

Number of moles of B_2H_6 in 27.66 g

$$= \frac{\text{Given mass}}{\text{Molar mass}} = \frac{27.66}{27.6} \approx 1$$

Now consider the equation

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

From the equation we can interpret that 3 moles of oxygen is required to burn 1 mole (i.e. 27.6 g) B_2H_6 completely.

Also consider the electrolysis reaction of water i.e.

$$H_2O \rightleftharpoons 2H^+ + O^{--}$$

$$2H^+ \xrightarrow[\text{Cathode}]{+2e^-} 2H \longrightarrow H_2\uparrow$$

$$O^{--} \xrightarrow[-2e^-]{\text{Anode}} O \xrightarrow{\text{2 such atoms}} O_2\uparrow$$

From the above equation it can be easily interpreted that in electrolysis of water for the production of 1 mole of oxygen from 1 mole of H_2O at anode 4 moles electrons are required.

Likewise for the production of 3 moles of O_2 $12(3\times4)$ moles of electrons will be needed.

So, the total amount of charge required to produce 3 moles of oxygen will be

$$12\times F \text{ or } 12\times96500$$

We know $Q = it$

So, $12\times96500 = 100\times t$ in seconds

or $\dfrac{12\times96500}{100\times3600} = t$ in hours $= 3.2$ hours

23 Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 u) **[JEE Main 2015]**

(a) 0g (b) 63.5g (c) 2g (d) 127g

Ans. ***(b)***

Given, $Q = 2F$

Atomic mass of Cu = 63.5 u

Valency of the metal $Z = 2$

We have, $CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

$$\underset{1\text{mol}}{Cu^{2+}} + \underset{\substack{2\text{ mol}\\ 2F}}{2e^-} \longrightarrow \underset{1\text{mol} = 63.5\text{ g}}{Cu}$$

Alternatively, $W = ZQ = \dfrac{E}{F}\cdot 2F = 2E$

$$= \frac{2\times63.5}{2} = 63.5$$

24 Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 Sm^{-1}. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in S mol^{-1} is **[JEE Main 2014]**

(a) 5×10^{-4} (b) 5×10^{-3}
(c) 5×10^{3} (d) 5×10^{2}

Ans. ***(a)***

For 0.2 M solution, $R = 50\ \Omega$

$$\kappa = 1.4\text{ S m}^{-1} = 1.4\times10^{-2}\text{ Scm}^{-1}$$

The resistivity of the solution is related to specific conductance by

$$\rho = \frac{1}{\kappa} = \frac{1}{1.4\times10^{-2}}\ \Omega\text{ cm}$$

It is known that, $R = \rho\dfrac{l}{a} \Rightarrow \dfrac{R}{\rho} = \dfrac{l}{a}$

$$\Rightarrow \quad \frac{l}{a} = R\times\frac{1}{\rho} = 50\times1.4\times10^{-2}\text{ cm}$$

For 0.5 M solution,

$R = 280\ \Omega$; $\kappa = ?$

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$$\frac{l}{a} = 50 \times 1.4 \times 10^{-2}\ \text{cm}$$

The specific conductance of the solution is given by

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a}$$

$$\kappa = \frac{1}{280} \times 50 \times 1.4 \times 10^{-2}$$

$$= 2.5 \times 10^{-3}\ \text{S cm}^{-1}$$

Now, the molar conductivity of the solution is given by

$$\Lambda_m = \frac{\kappa \times 1000}{\text{M}} = \frac{2.5 \times 10^{-3} \times 1000}{0.5}$$

$$= 5.5\ \text{cm}^2\,\text{mol}^{-1} = 5 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

Hence, the molar conductivity of 0.5 M solution of the electrolyte is $5 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$.

25 The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_c and λ_∞, respectively. The correct relationship between λ_c and λ_∞ is given as **[JEE Main 2014]**

(a) $\lambda_c = \lambda_\infty + (B)C$ (b) $\lambda_c = \lambda_\infty - (B)C$
(c) $\lambda_c = \lambda_\infty - (B)\sqrt{C}$ (d) $\lambda_c = \lambda_\infty + (B)\sqrt{C}$

Ans. ***(c)***

Debye-Huckel Onsager equation can be written as

$$\lambda_c = \lambda_\infty - (B)\sqrt{C}$$

Where,

λ_c = Molar conductivity of the solution at certain concentration

λ_∞ = Limiting molar conductivity

C = Concentration

B = Constant that depends on temperature, charges on the ions and dielectric constant as well as viscosity of the solution

26 Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.3 S m^{-1}. If resistance of the 0.4M solution of the same electrolyte is 260 Ω, its molar conductivity is **[AIEEE 2011]**

(a) 6250 S m^2 mol^{-1}
(b) 6.25×10^{-4} S m^2 mol^{-1}
(c) 625×10^{-4} S m^2 mol^{-1}
(d) 62.5 S m^2 mol^{-1}

Ans. ***(b)***

For 0.2 M solution,

Specific conductance (κ)

$$= \text{Conductance}\left(\frac{1}{R}\right) \times \text{Cell constant}\ (l/a)$$

$$\Rightarrow \quad \kappa = \frac{1}{50} \times \frac{l}{a} = 1.3\ \text{S m}^{-1}$$

$$\Rightarrow \quad \frac{l}{a} = 1.3 \times 50\ \text{m}^{-1}$$

$$\frac{l}{a} = 1.3 \times 50 \times 10^{-2}\ \text{cm}^{-1}$$

For 0.4 M solution, $R = 260\ \Omega$

$$R = \rho\frac{l}{a} \Rightarrow \frac{1}{\rho} = \kappa = \frac{1}{R} \times \frac{l}{a}$$

$$\kappa = \frac{1}{260} \times 1.3 \times 50 \times 10^{-2}\ \text{S cm}^{-1}$$

Molar conductivity of the solution is given by

$$\Lambda_m = \frac{\kappa \times 1000}{\text{M}}$$

$$= \frac{1}{260} \times \frac{1.3 \times 50 \times 10^{-2} \times 1000}{4}$$

$$= 6.25\ \text{S cm}^2\ \text{mol}^{-1}$$

$$= 6.25 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

27 The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below

$\Lambda^\circ_{CH_3COONa} = 91.0\ \text{S cm}^2/\text{equiv}$
$\Lambda^\circ_{HCl} = 426.2\ \text{S cm}^2/\text{equiv}$

What additional information/ quantity one needs to calculate Λ° of an aqueous solution of acetic acid ? **[AIEEE 2007]**

(a) Λ° of NaCl
(b) Λ° of CH_3COOK
(c) The limiting equivalent conductance of H^+ ($\lambda^\circ_{H^+}$)
(d) Λ° of chloroacetic acid ($ClCH_2COOH$)

Ans. ***(a)***

Molar conductivity of aqueous CH_3COOH solution can be calculated from Kohlraush's law as

$$\lambda^\circ_{CH_3COOH} = \lambda^\circ_{CH_3COONa} + \lambda^\circ_{HCl} - \lambda^\circ_{NaCl}$$

Hence, for determining the molar conductivity of CH_3COOH solution, λ°_{NaCl} is required.

28 Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.2 M of the same solution is 520 Ω. The molar conductivity of 0.2 M solution of the electrolyte will be **[AIEEE 2006]**

(a) 124×10^{-4} S m^2 mol^{-1}
(b) 1240×10^{-4} S m^2 mol^{-1}
(c) 1.24×10^{-4} S m^2 mol^{-1}
(d) 12.4×10^{-4} S m^2 mol^{-1}

Ans. ***(d)***

For 0.1 M solution

$$R = 100\ \Omega$$

$$\Rightarrow \quad \kappa = \frac{1}{R}\left(\frac{l}{a}\right)$$

$$\frac{l}{a}(\text{cell constant}) = 1.29 \times 100\ \text{m}^{-1}$$

For 0.2 M solution

Given, $R = 520\ \Omega$; C = 0.2 M

μ (molar conductivity) = ?

Molar conductivity,

$$\Lambda_m = \frac{\kappa \times 1000}{\text{M}}$$

[κ can be calculated as $\kappa = \frac{1}{R}\left(\frac{l}{a}\right)$, now cell constant is known]

Hence, $\Lambda_m = \frac{1}{520} \times 129 \times \frac{1000}{0.2} \times 10^{-6}\ \text{m}^3$

$$= 12.4 \times 10^{-4}\ \text{Sm}^2\ \text{mol}^{-1}$$

29 The molar conductivities Λ°_{NaOAc} and Λ°_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2S cm^2/mol, respectively. To calculate Λ°_{HOAc}, the additional value required is **[AIEEE 2006]**

(a) $\Lambda^\circ_{H_2O}$ (b) Λ°_{KCl}
(c) Λ°_{NaOH} (d) Λ°_{NaCl}

Ans. ***(d)***

According to Kohlrausch's law

$$[\text{NaOAc} = \text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O}^-\text{Na}^+]$$

$$\lambda^\circ_{CH_3COOH} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} \quad \ldots(i)$$

$$\lambda^\circ_{HCl} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} \quad \ldots(ii)$$

$$\lambda^\circ_{CH_3COONa} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+} \quad \ldots(iii)$$

Thus, on adding Eqs. (ii) and (iii), if $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are subtracted, we can obtained the value of λ°_{HOAc}. Thus, additional value required is λ°_{NaCl}.

30 The highest electrical conductivity from the following aqueous solutions is of **[AIEEE 2005]**

(a) 0.1 M difluoroacetic acid
(b) 0.1 M fluoroacetic acid
(c) 0.1 M chloroacetic acid
(d) 0.1 M acetic acid

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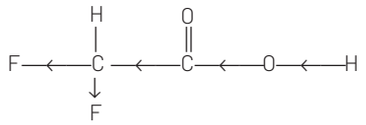
Ans. ***(a)***

Fluoro group causes negative inductive effect increasing ionisation. Thus, 0.1 M difluoroacetic acid has highest electrical conductivity.



31

Electrolyte	KCl	KNO_3	HCl	NaOAc	NaCl
Λ^∞ (S cm^2 mol^{-1})	149.9	145.0	426.2	91.0	126.5

Calculate Λ^∞_{HOAc} using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C.

[AIEEE 2005]

(a) 217.5 (b) 390.7
(c) 552.7 (d) 517.2

Ans. ***(b)***

$$\Lambda^\infty_{AcOH} = \Lambda^\infty_{AcONa} + \Lambda^\infty_{HCl} - \Lambda^\infty_{NaCl}$$
$$= 91.0 + 426.2 - 126.5 = 390.7$$

32 Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (atomic mass = 27 u; 1 Faraday = 96,500 C). The cathode reaction is

$$Al^{3+} + 3e^- \longrightarrow Al^0$$

To prepare 5.12 kg of aluminium metal by this method would require **[AIEEE 2005]**

(a) 5.49×10^1 C of electricity
(b) 5.49×10^4 C of electricity
(c) 1.83×10^7 C of electricity
(d) 5.49×10^7 C of electricity

Ans. ***(d)***

$$Al^{3+} + 3e^- \longrightarrow Al$$
$$w = zQ$$

where, w = amount of metal
$= 5.12\ kg = 5.12 \times 10^3\ g$
z = electrochemical equivalent

$$= \frac{\text{equivalent weight}}{96500}$$
$$= \frac{\text{atomic mass}}{\text{electrons} \times 96500}$$
$$= \frac{27}{3 \times 96500}$$

$$5.12 \times 10^3 = \frac{27}{3 \times 96500} \times Q$$

$$Q = \frac{5.12 \times 10^3 \times 3 \times 96500}{27}\ C$$
$$= 5.49 \times 10^7\ C$$

33 The limiting molar conductivities $\Lambda°$ for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1}, respectively. The $\Lambda°$ for NaBr is **[AIEEE 2004]**

(a) 128 S $cm^2 mol^{-1}$ (b) 176 S $cm^2 mol^{-1}$
(c) 278 S $cm^2 mol^{-1}$ (d) 302 S $cm^2 mol^{-1}$

Ans. ***(a)***

By Kohlrausch's law.

$$\Lambda°_{NaBr} = \Lambda°_{NaCl} + \Lambda°_{KBr} - \Lambda°_{KCl}$$
$$= 126 + 152 - 150$$
$$= 128\ S\ cm^2\ mol^{-1}$$

34 When during electrolysis of a solution of $AgNO_3$, 9650 C of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be **[AIEEE 2003]**

(a) 1.08 g (b) 10.8 g
(c) 21.6 g (d) 108 g

Ans. ***(b)***

$$Ag^+ + e^- \longrightarrow Ag$$

Number of moles of Ag $= \frac{9650}{96500}$

$$= \frac{1}{10}\ \text{moles}$$

$$Ag^+ + e^- \longrightarrow Ag$$

$\therefore$ Mass of Ag produced $= \frac{1}{10} \times 108 = 10.8\ g$

35 Conductivity (Seimen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then constant of proportionality is expressed in **[AIEEE 2002]**

(a) S m mol^{-1} (b) S^2 m^2 mol^{-2}
(c) S m^2 mol^{-1} (d) S^2 m^2 mol

Ans. ***(c)***

$$S \propto \text{area}\,(m^2) \propto \text{conc}\,(mol/m^3)$$
$$\propto \frac{1}{\text{length}}\,(m^{-1})$$
$$S = \kappa m^2\ \frac{mol}{m^3}\ m^{-1}$$

$\Rightarrow$ $\kappa = S\ mol^{-1}\ m^2$

TOPIC 2
Electrochemical Series, Electrode Potential and EMF

36 Consider the following cell reaction,

$$Cd(s) + Hg_2SO_4(s) + \frac{9}{5}H_2O(l) \rightleftharpoons CdSO_4 \cdot \frac{9}{5}H_2O(s) + 2Hg(l)$$

The value of E°_{cell} is 4.315 V at 25°C. If $\Delta H° = -825.2$ kJ mol^{-1}, the standard entropy change $\Delta S°$ in J K^{-1} is ..... (Nearest integer)

[Given, Faraday constant = 96487 C mol^{-1}] **[2021, 31 Aug Shift-I]**

Ans. ***(25)***

$$\Delta G° = \Delta H° - T\Delta S° \quad ...(i)$$

where, $\Delta G°$ = standard Gibb's free energy change
$\Delta H°$ = standard change in enthalpy
$\Delta S°$ = standard entropy change

Also, $\Delta G° = -nFE°$

where, n = number of electrons
F = Faraday constant
$E°$ = standard cell potential

$\therefore$ Equation (i) is,

$$-nFE° = \Delta H° - T\Delta S°$$
$$-nFE° - \Delta H° = -T\Delta S°$$
$$\Rightarrow \quad \Delta S° = \frac{nFE° + \Delta H°}{T}$$
$$= \frac{(2 \times 96487\ C\ mol^{-1} \times 4.315\ V) + (-825.2\ kJ/mol)}{298\ K}$$
$$= \frac{832.682 \times 10^3\ J\ mol - 825.2 \times 10^3\ J/mol}{298\ K}$$
$$= 25.11\ J/K\ mol$$

37 For the cell

$Cu(s)|Cu^{2+}(aq)(0.1\ M)||\ Ag^+(aq)(0.01M)|\ Ag(s)$

the cell potential, $E_1 = 0.3095$ V

For the cell,

$Cu(s)|Cu^{2+}(aq)(0.01\ M)||\ Ag^+(aq)(0.001M)|\ Ag(s)$

the cell potential
$= \ldots\ldots\ldots\ldots \times 10^{-2}$ V.

(Round off the nearest integer).

$$\left[\text{Use}: \frac{2.303RT}{F} = 0.059\right]$$

[2021, 27 July Shift-II]

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Ans. *(28)*

Cell reaction,

$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Ag^{2+}]^2}$$

$$E_1 = 0.3095 = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{(0.1)}{(0.01)^2}$$

$$E^\circ_{cell} = 0.3095 + \frac{0.0591}{2}\log(1000)$$

$$= 0.3095 + \frac{0.0591}{2}\log 10^3$$

$$E^\circ_{cell} = 0.3095 + \frac{0.0591}{2}\times 3 \quad \ldots(i)$$

$$E_2 = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{(0.01)}{(0.001)^2}$$

$$E_2 = E^\circ_{cell} - \frac{0.0591}{2}\log 10000$$

$$= E^\circ_{cell} - \frac{0.0591}{2}\log 10^4$$

$$E_2 = E^\circ_{cell} - \frac{0.0591}{2}\times 4$$

From Eq. (i),

$$E_2 = 0.3095 + \frac{0.0591}{2}\times 3 - \frac{0.0591}{2}\times 4$$

$$= 0.3095 - \frac{0.0591}{2} = 0.3095 - 0.0295$$

$$= 0.28 = 28\times 10^{-2}\ V$$

38 For the galvanic cell,

$Zn(s) + Cu^{2+}(0.02\ M) \longrightarrow Zn^{2+}(0.04M) + Cu(s)$,

$E_{Cell} = \ldots\ldots\ldots \times 10^{-2}$ V.

(Nearest integer)

[Use $E^\circ_{Cu/Cu^{2+}} = -0.34$ V, $E^\circ_{Zn/Zn^{2+}} = +0.76$ V, $\frac{2.303RT}{F} = 0.059$ V]

[2021, 26 Aug Shift-II]

Ans. *(109)*

Cell reaction,

$$\underset{0.02\ M}{Cu^{2+}(aq)} + Zn(s) \rightleftharpoons Cu(s) + \underset{0.04\ M}{Zn^{2+}(aq)}$$

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}$$

$$= 0.34 - (-0.75) = 1.1\ V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.1 - \frac{0.059}{2}\log\frac{[0.04]}{[0.02]}$$

$$= 1.1 - 0.03\log 2 = 1.1 - 0.03\times 0.30$$

$$= 1.09\ V = 109\times 10^{-2}\ V$$

∴ Answer is 109.

39 These are physical properties of an element.

A. Sublimation enthalpy

B. Ionisation enthalpy

C. Hydration enthalpy

D. Electron gain enthalpy

The total number of above properties that affect the reduction potential is .....

(Integer answer)

[2021, 26 Aug Shift-I]

Ans. *(3)*

The physical properties of an element is affected by sublimation enthalpy, ionisation enthalpy and hydration enthalpy as these 3 enthalpies will affect the reduction potential.

40 Consider the cell at 25° C

$Zn|Zn^{2+}(aq), (1M)||Fe^{3+}(aq), Fe^{2+}(aq)|Pt(s)$

The fraction of total iron present as Fe^{3+} ion at the cell potential of 1.500 V is $x\times 10^{-2}$. The value of x is ..... . (Nearest integer)

(Given, $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V, $E^\circ_{Zn^{2+}/Zn} = -0.76$ V)

[2021, 25 July Shift-I]

Ans. *(24)*

Reaction cell

$Zn|Zn^2(aq), (1M)||Fe^{3+}(aq)|, Fe^{2+}(aq), Pt(s)$

(Anode) $Zn \longrightarrow Zn^{2+} + 2e^-$

(Cathode) $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$

Overall $Zn + 2Fe^{3+} \longrightarrow Zn^{2+} + 2Fe^{2+}$

Given values are :

Reduction potential of Fe(III) = 0.77 V

Reduction potential of Zn(II) = −0.76 V

$$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Zn^{2+}/Zn}$$

$$= 0.77 - (-0.76)$$

$$= 1.53\ V$$

Using Nernst equation,

$$E_{cell} = E^\circ{}_{cell} - \frac{0.0591}{n}\log\frac{[P]}{[R]}$$

$$1.50 = 1.53 - \frac{0.0591}{2}\log\left(\frac{Fe^{2+}}{Fe^{3+}}\right)^2$$

$$\log\left(\frac{Fe^{2+}}{Fe^{3+}}\right) = \frac{0.03}{0.06} = \frac{1}{2}$$

$$\frac{[Fe^{2+}]}{[Fe^{3+}]} = 10^{1/2} = \sqrt{10}$$

$$\frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{1}{\sqrt{10}}$$

$$\frac{[Fe^{3+}]}{[Fe^{2+}] + [Fe^{3+}]} = \frac{1}{1+\sqrt{10}} = \frac{1}{4.16}$$

$$= 0.2402 = 24\times 10^{-2}$$

So, the value of x is 24.

41 Assume a cell with the following reaction

$Cu(s) + 2Ag^+(1\times 10^{-3}M) \longrightarrow Cu^{2+}(0.250M) + 2Ag(s)$,

$E^\ominus_{cell} = 2.97$ V

E_{cell} for the above reaction is ..... V.

(Nearest integer)

[Given : $\log 2.5 = 0.3979$, $T = 298$ K]

[2021, 22 July Shift -II]

Ans. *(3)*

Given $E^\circ{}_{cell} = 2.97$ V

Now, balanced the equation,

$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$ (oxidation)

$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$ (reduction)

Overall:

$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

$n = 2$ (for 2 electrons)

$E^\circ_{cell} = 2.97$ V

Using nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$= 2.97 - \frac{0.0591}{2}\log\frac{0.250}{(10^{-3})^2}$$

$$= 2.81 \approx 3 \text{ (approx.)}$$

Hence, E°_{cell} of the reaction is 3V.

42 The molar conductivities at infinite dilution of barium chloride, sulphuric acid and hydrochloric acid are 280, 860 and 426 $Scm^2\ mol^{-1}$ respectively. The molar conductivity at infinite dilution of barium sulphate is ... $S\ cm^2\ mol^{-1}$ (Round off to the nearest Integer).

[2021, 18 March Shift-II]

Ans. *(288)*

Molar conductivity of $BaCl_2$ = 280 Scm^2mol^{-1}

Molar conductivity of H_2SO_4 = 860 Scm^2mol^{-1}

Molar conductivity of HCl = 426 Scm^2mol^{-1}

Molar conductivity of $BaSO_4$ = ?

From Kohlrausch's law,

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$\Lambda_m^\infty(BaSO_4) = \lambda_m^\infty(Ba^{2+}) + \lambda_m^\infty(SO_4^{2-})$

$\Lambda_m^\infty(BaSO_4) = \Lambda_m^\infty(BaCl_2) + \Lambda_m^\infty(H_2SO_4) - 2\Lambda_m^\infty(HCl)$

On putting given values we get,

$= 280 + 860 - 2(426)$

$= 288\ Scm^2\ mol^{-1}$

43 For the reaction,

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$

The magnitude of the standard molar Gibbs free energy change, $\Delta_r G_m^\circ = -$ ..... kJ (Round off to the nearest integer).

$\left[E^\circ_{Fe^{2+}/Fe(s)} = -0.440\ V;\ E^\circ_{I_2/2I^-} = 0.539\ V;\ E^\circ_{Fe^{3+}/Fe(s)} = -0.036\ V\right.$

$\left. F = 96500\ C\right]$

[2021, 18 March Shift-I]

Ans. ***(45)***

Given reaction is

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$

Now, $Fe^{3+} \xrightarrow{E_1^\circ} Fe^{2+} \xrightarrow{E_2^\circ} Fe$, $Fe^{3+} \xrightarrow{E_3^\circ} Fe$

$nE_1^\circ + nE_2^\circ = nE_3^\circ$

[n = number of electron transferred]

$1E_1^\circ + 2E_2^\circ = 3E_3^\circ$

$E^\circ_{Fe^{3+}/Fe^{2+}} + 2E^\circ_{Fe^{2+}/Fe\,(s)} = 3E^\circ_{Fe^{3+}/Fe\,(s)}$

$E^\circ_{Fe^{3+}/Fe^{2+}} + (-0.440) \times 2 = (-0.036) \times 3$

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.772\ V$

$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode}$

$= 0.772 - 0.539 = 0.233\ V$

Using standard Gibb's free energy,

$\Delta G^\circ = nFE^\circ_{cell} = +2 \times 96500 \times 0.233$

$\Delta G^\circ = 44969\ J = 44.9\ kJ = 45\ kJ$

44 Emf of the following cell at 298 K in V is $x \times 10^{-2}$, $Zn\,|\,Zn^{2+}\,(0.1\ M)\ ||\ Ag^+\,(0.01\ M)\,|\,Ag$

The value of x is ..... .
(Rounded off to the nearest integer).

[Given, $E^\circ_{Zn^{2+}/Zn} = -0.76\ V$, $E^\circ_{Ag^+/Ag} = +0.80\ V$, $\frac{2.303RT}{F} = 0.059$]

[2021, 26 Feb Shift-II]

Ans. ***(147)***

$Zn|Zn^{2+}(0.1M)\ ||\ Ag^+(0.01M)|Ag$

Cell reaction :

$Zn(s) + \underset{0.01M}{2Ag^+} \rightleftharpoons \underset{0.1M}{Zn^{2+}} + 2Ag(s)$

$\Rightarrow \quad Q = \frac{[Zn^{2+}]\,[Ag]^2}{[Zn]\,[Ag^+]^2} = \frac{0.1 \times 1^2}{1 \times (0.01)^2} = 10^3$

$n = 2$

and $E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Zn^{2+}/Zn}$

$= 0.8 - (-0.76) = 1.56\ V$

$\Rightarrow \quad E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log Q$

$= 1.56 - \frac{0.059}{2}\log 10^3$

$= 1.4715\ V$

$= 147.15 \times 10^{-2}\ V$

$= 147 \times 10^{-2}\ V$

$= x \times 10^{-2}\ V$

$x = 147$

45 Copper reduces NO_3^- into NO and NO_2 depending upon the concentration of HNO_3 in solution. (Assuming fixed $[Cu^{2+}]$ and $p_{NO} = p_{NO_2}$), the HNO_3 concentration at which the thermodynamic tendency for reduction of NO_3^- into NO and NO_2 by copper is same is 10^x M. The value of $2x$ is ..... .
(Rounded off to the nearest integer) **[2021, 25 Feb Shift-II]**

Ans. ***(4)***

Cell-I ($HNO_3 \longrightarrow NO$)

$3Cu + 2NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$

$Q_1 = \frac{[Cu^{2+}]^3 \times (p_{NO})^2}{[NO_3^-]^2 \times [H^+]^8}$

$\because \quad E_1^\circ = 0.96 - (-0.34) = 1.3\ V$

$E_1 = 1.3 - \frac{0.059}{6}\log Q_1$

Cell-II ($HNO_3 \rightarrow NO_2$)

$Cu + 2NO_3^- + 4H^+ \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$

$Q_2 = \frac{[Cu^{2+}] \times (p_{NO_2})^2}{[NO_3^-]^2 \times [H^+]^4}$

$\because \quad E_2^\circ = 0.79 - (-0.34)V = 1.13\ V$

$E_2 = 1.13 - \frac{0.059}{2}\log Q_2$

Now, $E_1 = E_2$

$1.3 - \frac{0.059}{6}\log Q_1 = 1.13 - \frac{0.059}{2}\log Q_2$

$0.17 = \frac{0.059}{6}[\log Q_1 - 3\log Q_2]$

$= \frac{0.059}{6}\log\frac{Q_1}{Q_2}$

$= \frac{0.059}{6}\log\frac{[Cu^{2+}]^3 \times (p_{NO})^2}{[NO_3^-]^2 \times [H^+]^8} \times \frac{[NO_3^-]^6 \times [H^+]^{12}}{[Cu^{2+}]^3 \times (p_{NO_2})^6}$

$= \frac{0.059}{6}\log\frac{[H^+]^4 \times [NO_3^-]^4}{(p_{NO_2})^4}$ [$\because p_{NO} = p_{NO_2}$]

$= \frac{0.059}{6}\log\frac{[HNO_3]^4}{(p_{NO_2})^4}$

Now, $p_{NO_2} \equiv [HNO_3]$

So, $0.17 = \frac{0.059}{6}\log[HNO_3]^8$

$= \frac{0.059}{6} \times 8\log[HNO_3]$

$\log[HNO_3] = 2.16$

$[HNO_3] = 10^{2.16}\ M = 10^x\ M$

$\therefore \quad x = 2.16$

$\Rightarrow \quad 2x = 2 \times 2.16 = 4.32 \simeq 4$

46 The magnitude of the change in oxidising power of the MnO_4^-/Mn^{2+} couple is $x \times 10^{-4}$ V, if the H^+ concentration is decreased from 1 M to 10^{-4} M at 25°C. (Assume concentration of MnO_4^- and Mn^{2+} to be same on change in H^+ concentration). The value of x is ..... (Rounded off to the nearest integer). $\left[\text{Given, } \frac{2.303\,RT}{F} = 0.059\right]$

[2021, 24 Feb Shift-II]

Ans. ***(3776)***

Reaction,

$MnO_4^- + H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$n = 5$

Applying Nernst equation,

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[P]}{[R]}$

or $E_{cell} = E^\circ_{cell} - \frac{0.0591}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-]}\left[\frac{1}{H^+}\right]^8$

(I) Given, $[H^+] = 1\ M$

$E_1 = E^\circ - \frac{0.0591}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-]}$

(II) Now, $[H^+] = 10^{-4}$ M

$E_2 = E^\circ - \frac{0.0591}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-]} \times \frac{1}{(10^{-4})^8}$

$\therefore |E_1 - E_2|$

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$$|E_1 - E_2| = \frac{0.0591}{5} \times 32 = 0.3776\ V$$
$$= 3776 \times 10^{-4}$$
$$x = 3776$$

47 The Gibbs energy change (in J) for the given reaction at $[Cu^{2+}] = [Sn^{2+}] =$ 1M and 298 K is

$Cu(s) + Sn^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Sn(s)$;

($E^\circ_{Sn^{2+}/Sn} = -0.16$ 0.16 V, $E^\circ_{Cu^{2+}/Cu} = 0.34$ V,

Take, $F = 96500\ C\ mol^{-1}$)

[2020, 2 Sep Shift-I]

Ans. ***(96500)***

$$Cu(s) + \underset{(1\,M)}{Sn^{2+}}(aq) \longrightarrow \underset{(1\,M)}{Cu^{2+}}(aq) + Sn(s)$$
$$E_{cell} = (E^\circ_{Sn^{2+}/Sn} - E^\circ_{Cu^{2+}/Cu}) - \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Sn^{2+}]}$$
$$= (-0.16 - 0.34) - \frac{0.0591}{2}\log\frac{1}{1} = -0.50\ V$$
$$\Delta G = -nF\,E^\circ_{cell} = -2 \times 96500 \times (-0.50)\ J$$
$$= 96500.00\ J$$

48 For the disproportionation reaction $2Cu^+(aq) \rightleftharpoons Cu(s) + Cu^{2+}(aq)$ at 298 K, ln K (where K is the equilibrium constant) is .....$\times 10^{-1}$.

Given : ($E^\circ_{Cu^{2+}/Cu^+} = 0.16$ V,

$E^\circ_{Cu^+/Cu} = 0.52$ V and $\frac{RT}{F} = 0.025$)

[2020, 2 Sep Shift-II]

Ans. ***(144)***

$$2Cu^+(aq) \rightleftharpoons Cu(s) + Cu^{2+}(aq)$$

For the cell reaction,

$$E^\circ_{cell} = E^\circ_{Cu^+/Cu} - E^\circ_{Cu^{2+}/Cu^+} = (0.52 - 0.16)$$
$$V = 0.36\ V$$
$$\Rightarrow \Delta G^\circ = -nF\,E^\circ_{cell}$$
$$\Rightarrow -RT\ln K = -nF\,E^\circ_{cell}$$
$$\Rightarrow \ln K = n \times \frac{E}{RT} \times E^\circ_{cell}$$
$$= 1 \times \frac{1}{0.025} \times 0.36$$
$$= 14.4 = 144 \times 10^{-1}$$

49 The photoelectric current from Na (work function, $w_0 = 2.3$ eV) is stopped by the output voltage of the cell $Pt(s)\,|H_2(g, 1\ bar)|$ HCl ($aq.$, pH = 1)$|AgCl(s)|\,Ag(s)$.

The pH of aqueous HCl required to stop the photoelectric current from K($w_0 = 2.25$ eV), all other conditions remaining the same, is ..... $\times 10^{-2}$ (to the nearest integer).

Given, $2.303\frac{RT}{F} = 0.06$ V;

$E^\circ_{AgCl|Ag|Cl^-} = 0.22$ V

[2020, 3 Sep Shift-I]

Ans. ***(58.3)***

$$Pt(s)\|H_2(g), 1\ bar\,|HCl(aq)(pH = 1)\| (Ag(s)\|AgCl)$$

Reaction involved :

$$\frac{1}{2}H_2 + AgCl(s) \longrightarrow Ag(s) + H^+ + Cl^-$$
$$E_{cell} = E_{Ag} = \left\{0.22 - \frac{0.06}{1}\log[H^+][Cl^-]\right\}$$
$$E_K = 0.22 - \frac{0.06}{1}\log[H^+][Cl^-]$$

For Na, $\frac{hc}{\lambda} = 2.3 - E_{Na}$ ...(i)

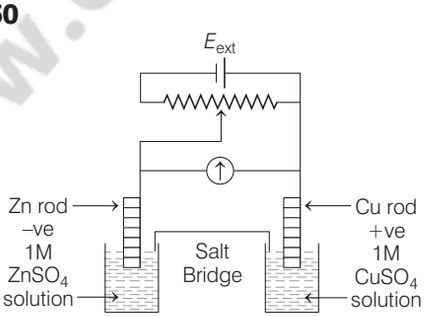
For K, $\frac{hc}{\lambda} = 2.25 - E_K$ ...(ii)

Equating (i) and (ii)

$$2.3\,E_{Na} = 2.25 - E_K$$
$$0.05 - 0.22 + 0.06\log(10^{-1})(10^{-1}) = -0.22 + 0.06\log[H^+][Cl^-]$$
$$5 + 6\log(10^{-2}) = 6\log[H^+]^2$$
$$-\frac{7}{12} = \log[H^+]$$
$$pH = +\frac{7}{12} = 0.5833$$
$$pH = x \times 10^{-2} = 58.3 \times 10^{-2}$$

So, value is 58.3.

50



$$E^\circ_{Cu^{2+}|Cu} = +0.34\ V$$
$$E^\circ_{Zn^{2+}|Zn} = -0.76\ V$$

Identify the incorrect statement from the options below for the above cell. **[2020, 4 Sep Shift-I]**

(a) If $E_{ext} > 1.1$ V, Zn dissolves at Zn electrode and Cu deposits at Cu electrode.

(b) If $E_{ext} = 1.1$ V, no flow of electrons or current occurs.

(c) If $E_{ext} > 1.1$ V, electrons flows from Cu to Zn.

(d) If $E_{ext} < 1.1$ V, Zn dissolves at anode and Cu deposits at cathode.

Ans. ***(a)***

Given, $E^\circ_{Cu^{2+}/Cu} = -0.34$ V

$E^\circ_{Zn^{2+}/Zn} = -0.76$ V

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}$$
$$= 0.34 - (-0.76)$$
$$= 1.10\ volt$$

Statement (a) is incorrect whereas all other statements are correct.

If $E_{ext} > 1.1$ V {act as electrolytic cell}

Cu → Anode

Zn → Cathode

If, $E_{ext} = 1.10$ V

Zn → Anode

Cu → Cathode

So, Zn dissolves at copper electrode and Cu at Zn electrode.

51 An oxidation-reduction reaction in which 3 electrons are transferred has a $\Delta G°$ of 17.37 kJ mol^{-1} at 25° C. The value of E°_{cell} (in V) is ..... $\times 10^{-2}$. (1 F = 96,500 C mol^{-1})

[2020, 5 Sep Shift-I]

Ans. ***(6)***

$\therefore \quad \Delta G^\circ = -nFE^\circ_{cell}$

Here, $\Delta G^\circ = 17.37$ kJ mol^{-1}

n = number of electrons

F = Faraday constant

= 96500 C /mol

$= 17.37 \times 1000\ J\ mol^{-1}$

$$17.37 \times 1000 = -3 \times 96500 \times E^\circ_{cell}$$
$$E^\circ_{cell} = \frac{17.37 \times 1000}{3 \times 96500}$$
$$E^\circ_{cell} = -0.06 = -6 \times 10^{-2}$$

52 For the given cell;

$Cu(s)|Cu^{2+}(C_1M)||Cu^{2+}(C_2M)|Cu(s)$

change in Gibbs energy (ΔG) is negative, if **[2020, 6 Sep Shift-II]**

(a) $C_1 = C_2$ (b) $C_2 = \frac{C_1}{\sqrt{2}}$

(c) $C_1 = 2C_2$ (d) $C_2 = \sqrt{2}\,C_1$

Ans. ***(d)***

Given, cell is

$Cu(s)|Cu^{2+}(C_1M)\,||\,Cu^{2+}(C_2M)|Cu(s)$

Gibbs free energy, $\Delta G = -nFE_{cell}$

ΔG is negative, if E_{cell} is positive, two half reaction are as follows for given cell reaction

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At anode $Cu(s) \longrightarrow Cu^{2+}(C_1) + 2e^-$
At cathode $Cu^{2+}(C_2) + 2e^- \longrightarrow Cu(s)$
Total cell reaction
$Cu^{2+}(C_2) \longrightarrow Cu^{2+}(C_1)$; $E^\circ_{cell} = 0$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log Q$$

$$E_{cell} = 0 - \frac{2.303RT}{nF}\log\left(\frac{C_1}{C_2}\right)$$

$E_{cell} > 0$; if $\frac{C_1}{C_2} < 1 \Rightarrow C_1 < C_2$

$C_2 = \sqrt{2}\, C_1$ is correct.

53 Given that the standard potentials ($E°$) of Cu^{2+}/Cu and Cu^+/Cu are 0.34 V and 0.522 V respectively, the $E°$ of Cu^{2+}/Cu^+ is

[2020, 7 Jan Shift-I]

(a) – 0.158 V (b) +0.158 V
(c) – 0.182 V (d) 0.182 V

Ans. ***(b)***

The half cell reactions are :
(1) $Cu^{2+} + 2e^- \rightleftharpoons Cu$; $E° = 0.34$ V
(2) $Cu^+ + e^- \rightleftharpoons Cu$; $E° = 0.522$ V
(3) $Cu^{2+} + e^- \rightleftharpoons Cu^+$; $E° = x$
As we know, $\Delta G° = -nFE$
∴ To obtain the $E°$ of required equation, subtract $\Delta G°$ of equation (2) from $\Delta G°$ of (1) as
$\Delta G°$ of (3) = $\Delta G°$ of (1) – $\Delta G°$ of (2)
or $-1 \times F \times x = (-2 \times F \times 0.34) - (-1 \times F \times 0.522)$

$$\therefore \quad x = 2 \times 0.34 - 0.522$$
$$= 0.68 - 0.522 = 0.158 \text{ V}$$

54 What would be the electrode potential for the given half-cell reaction at pH = 5 ? ..... .

$2H_2O \rightarrow O_2 + 4H^\oplus + 4e^-$;
$E°_{red} = 1.23$ V
($R = 8.314$ J mol^{-1} K^{-1}; Temp = 298 K; oxygen under std. atm. pressure of 1 bar)

[2020, 8 Jan Shift-I]

Ans. ***(0.94)***

Given, $E°_{red} = 1.23$ V
But as the given half cell reaction is an oxidation reaction. Therefore,

$$E°_{oxi} = -E°_{red} = -1.23 \text{ V} \Rightarrow n = 4$$
$$T = 298 \text{ K}$$

$\Rightarrow$ pH = 5
$\Rightarrow$ $[H^+] = 10^{-5}$

By Nernst equation, at 298 K :

$$E = E° - \frac{0.0591}{n}\log Q \quad [\because Q = p_{O_2} \times [H^+]^4]$$

$$= -1.23 - \frac{0.0591}{4}\log 1 \times (10^{-5})^4$$
$$= -1.23 - 0.0591\left(\frac{1}{4}\log 10^{-20}\right)$$
$$= -1.23 - 0.0591 \times 5 \log 10$$
$$= -1.23 - (0.0591 \times -5)$$
$$= -1.23 + 0.295$$
$$= -0.935 \text{ V} \approx -0.94 \text{ V}$$

55 For an electrochemical cell $Sn(s)|Sn^{2+}(aq, 1\text{ M})||Pb^{2+}(aq, 1\text{ M})|Pb(s)$ the ratio $\frac{[Sn^{2+}]}{[Pb^{2+}]}$ when this cell attains equilibrium is ..... .

$$\left(\text{Given : } E°_{Sn^{2+}|Sn} = -0.14 \text{ V}, \; E°_{Pb^{2+}|Pb} = -0.13 \text{ V}, \frac{2.303RT}{F} = 0.06\right)$$

[2020, 8 Jan Shift-II]

Ans. ***(2.15)***

(exact value -2.154)
Cell notation :
$Sn(s)|Sn^{2+}(aq; 1\text{ M})||Pb^{2+}(aq; 1\text{ M})|Pb(s)$
Cell reaction :
$Sn(s) + Pb^{2+}(aq) \rightleftharpoons Pb(s) + Sn^{2+}(aq)$

$$\text{Equilibrium constant } (K) = \frac{[Sn^{2+}]}{[Pb^{2+}]}$$

$\Rightarrow$ unknown
$E°_{Cell} = E°_{Cathode} - E°_{Anode}$
$= (-0.13 \text{ V}) - (-0.14 \text{ V}) = 0.01$ V
From Nernst equation,

$$E° = \frac{2.303RT}{nF}\log K = \frac{0.06}{n}\log K$$

$$\therefore \quad \log K = \frac{nE°}{0.06}; (n = 2)$$
$$= \frac{2 \times 0.01}{0.06} = 0.33 \text{ or } \frac{1}{3}$$
$$K = 10^{0.33} \text{ or}$$
$$= \sqrt[3]{10} = 2.154 \approx 2.15$$

The value may range from 2.13 to 2.17.

56 Given, that $E^\ominus_{O_2/H_2O} = +1.23$V;

$E^\ominus_{S_2O_8^{2-}/SO_4^{2-}} = 2.05$V;
$E^\ominus_{Br_2/Br^s} = +1.09$V,
$E^\ominus_{Au^{3+}/Au} = +1.4$V
The strongest oxidising agent is

[2019, 8 April Shift-I]

(a) Au^{3+} (b) O_2
(c) $S_2O_8^{2-}$ (d) Br_2

Ans. ***(c)***

Higher the standard reduction potential ($E°_{M^{n+}/M}$), better is oxidising agent.
Among the given, $E°_{S_2O_8^{2-}/SO_4^{2-}}$ is highest, hence $S_2O_8^{2-}$ is the strongest oxidising agent.
The decreasing order of oxidising agent among the given option is as follows:
$S_2O_8^{2-} > Au^{3+} > O_2 > Br_2$

57 Calculate the standard cell potential (in V) of the cell in which following reaction takes place

$Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Given that, $E°_{Ag^+/Ag} = x$ V,
$E°_{Fe^{2+}/Fe} = y$ V
$E°_{Fe^{3+}/Fe} = z$ V

[2019, 8 April Shift-II]

(a) $x + 2y - 3z$ (b) $x - y$
(c) $x + y - z$ (d) $x - z$

Ans. ***(a)***

$Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

$$\therefore E°_{cell} = E°_{Ag^+/Ag} - E°_{Fe^{3+}/Fe^{2+}}$$
$$= x \text{ V} - E°_{Fe^{3+}/Fe^{2+}} \quad \ldots(i)$$

Now, for two half-cells

(i) $Fe^{2+} + 2e^- \longrightarrow Fe$;
$E°_{Fe^{2+}/Fe} = E°_1 = y$ V
$\Delta G°_2 = -2FE°_1$

(ii) $Fe^{3+} + 3e^- \longrightarrow Fe$;
$E°_{Fe^{3+}/Fe} = E°_2 = z$ V
$\Delta G°_2 = -3FE°_2$

So, $Fe^{3+} + e^- \longrightarrow Fe^{2+}$;
$E°_{Fe^{3+}/Fe^{2+}} = E°_3 = ?$
; $\Delta G°_3 = -1 \times FE°_3$

Again, $\Delta G°_3 = \Delta G°_2 - \Delta G°_1$
$\Rightarrow$ $-FE°_3 = -3FE°_2 - (-2FE°_1)$
$\Rightarrow$ $-E°_3 = 2E°_1 - 3E°_2$
$\Rightarrow$ $E°_3 = 3E°_2 - 2E°_1$
$\Rightarrow$ $E°_{Fe^{3+}/Fe^{2+}} = (3z - 2y)$ V

So, from equation (i)

$$E°_{cell} = xV - (3z - 2y) \text{ V}$$
$$= (x - 3z + 2y) \text{ V}$$

58 The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$, $E° = 2$ V at 298 K

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(Faraday's constant, F = 96000 C mol^{-1}) **[2019, 9 April Shift-I]**

(a) 384 (b) 192
(c) –384 (d) –192

Ans. ***(c)***

Key Idea Gibbs energy of the reaction is related to $E°_{cell}$ by the following formula

$\Delta G^{\circ} = -nFE°_{cell}$

ΔG° = Gibbs energy of cell

nF = amount of charge passed

E = EMF of a cell

Given reaction is,

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

$E^{\circ}_{cell} = 2.0\ V; F = 96000\ C; n = 2$

To find the value of ΔG° (kJ mol), we use the formula

$\Delta G^{\circ} = -nFE^{\circ}_{cell}$

$\Delta G^{\circ} = -2 \times 96000 \times 2 = -384000\ J/mol$

In terms of kJ/mol, $\Delta G^{\circ} = \frac{-384000}{1000}$

$= -384\ kJ/mol$

59 Given,

$Co^{3+} + e^- \longrightarrow Co^{2+}; E° = +1.81\ V$

$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}; E° = +1.67\ V$

$Ce^{4+} + e^- \longrightarrow Ce^{3+}; E° = +1.61\ V$

$Bi^{3+} + 3e^- \longrightarrow Bi; E° = +0.20\ V$

Oxidising power of the species will increase in the order **[2019, 12 April Shift-I]**

(a) $Ce^{4+} < Pb^{4+} < Bi^{3+} < Co^{3+}$
(b) $Bi^{3+} < Ce^{4+} < Pb^{4+} < Co^{3+}$
(c) $Co^{3+} < Ce^{4+} < Bi^{3+} < Pb^{4+}$
(d) $Co^{3+} < Pb^{4+} < Ce^{4+} < Bi^{3+}$

Ans. ***(b)***

Key Idea Negative $E°$ means that redox couple is weaker oxidising agent than H^+/H_2 couple. Positive $E°$ means that redox couple is a stronger oxidising agent than H^+/H_2 couple

Given,

$Co^{3+} + e^- \longrightarrow Co^{2+}; E° = +1.81\ V$

$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}; E° = +1.67\ V$

$Ce^{4+} + e^- \longrightarrow Ce^{3+}; E° = +1.61\ V$

$Bi^{3+} + 3e^- \longrightarrow Bi; E° = +0.20\ V$

Oxidising power of the species increases in the order of $Bi^{3+} < Ce^{4+} < Pb^{4+} < Co^{3+}$.

Higher the emf value, stronger the oxidising power. The maximum value of emf is possessed by Co^{3+}. Hence, it has maximum oxidising power. Whereas Bi^{3+} possess the lowest emf value. Hence, it has minimum oxidising power.

60 If the standard electrode potential for a cell is 2V at 300 K, the equilibrium constant (K) for the reaction,

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ at 300 K is approximately ($R = 8\ JK^{-1}mol^{-1}$, F = 96000 C mol^{-1})

(a) e^{-160} (b) e^{160} (c) e^{-80} (d) e^{320} **[2019, 9 Jan Shift-II]**

Ans. ***(b)***

The relationship between standard electrode potential ($E°$) and equilibrium constant (K) of the cell reaction,

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

can be expressed as,

$E° = \frac{RT}{nF} \ln K \Rightarrow K = e^{nFE°/RT}$

Given, $n = 2, F = 96000\ C\ mol^{-1}$

$E° = 2\ V, R = 8\ JK^{-1}\ mol^{-1}, T = 300\ K$

$\therefore \quad K = e^{\frac{2 \times 96000 \times 2}{8 \times 300}} = e^{160}$

61 Consider the following reduction processes:

$Zn^{2+} + 2e^- \rightarrow Zn(s);\ E° = -0.76\ V$

$Ca^{2+} + 2e^- \rightarrow Ca(s);\ E° = -2.87\ V$

$Mg^{2+} + 2e^- \rightarrow Mg(s);\ E° = -2.36\ V$

$Ni^{2+} + 2e^- \rightarrow Ni(s);\ E° = -0.25\ V$

The reducing power of the metals increases in the order

(a) Zn < Mg < Ni < Ca
(b) Ni < Zn < Mg < Ca
(c) Ca < Zn < Mg < Ni
(d) Ca < Mg < Zn < Ni **[2019, 10 Jan Shift-I]**

Ans. ***(b)***

Reducing power of an element $\propto \frac{1}{\text{Standard reduction potential}}$

Here, $E°_{M^{2+}/M}$ values of the given metals are as,

Metals	Ni	Zn	Mg	Ca
E°(V)	–0.25	–0.76	–2.36	–2.87

$\longrightarrow$ Reducing power

Thus, the correct order of increasing reducing power of the given metal is,

Ni < Zn < Mg < Ca.

62 In the cell,

$Pt(s)|H_2(g, 1\ bar)|HCl(aq)|AgCl(s)|Ag(s)|Pt(s)$ the cell potential is 0.92 V when a 10^{-6} molal HClsolution is used. The standard electrode potential of $(AgCl/Ag, Cl^-)$ electrode is

$\left\{\text{Given, } \frac{2.303RT}{F} = 0.06\ V \text{ at } 298\ K\right\}$ **[2019, 10 Jan Shift-II]**

(a) 0.40 V (b) 0.20 V
(c) 0.94 V (d) 0.76 V

Ans. ***(b)***

It is an electrochemical cell. The overall cell reaction can be written, as

$\underset{(1\ bar)}{H_2(g)} + 2AgCl(s) \longrightarrow \underset{(10^{-6}\ M)}{2HCl(aq)} + 2Ag(s)$

(i) According to Nernst equation,

$E_{cell} = (E°_{cathode} - E°_{anode}) - \frac{2.303 \times RT}{n \times F} \log \frac{[HCl]^2[Ag]^2}{p_{H_2}[AgCl]^2}$

Here, (i) $E°_c = E°_{AgCl/Ag, Cl^-} = E°_{cathode}$

(ii) $E°_{anode} = E°_{2H^+/H_2} = 0.00\ V$

(Standard hydrogen electrode)

$\Rightarrow 0.92 = (E°_c - 0) - 0.06 \times \log \frac{(10^{-6})^2 \times 1^2}{1 \times 1^2}$

$= E°_c + 0.06 \times 6 \times 2$

$\Rightarrow E°_c = 0.92 - 0.72$

$= 0.20\ V$

Note 10^{-6} molal HCl is a very dilute solution.

So, 10^{-6} m $\simeq 10^{-6}$ M

63 For the cell,

$Zn(s)|Zn^{2+}(aq)||M^{x+}(aq)|M(s)$,

different half cells and their standard electrode potentials are given below.

$M^{x+}(aq)/M(s)$	$Au^{3+}(aq)/Au(s)$	$Ag^+(aq)/Ag(s)$	$Fe^{3+}(aq)/Fe^{2+}(aq)$	$Fe^{2+}(aq)/Fe(s)$
$E°_{M^{x+}/M}/V$	1.40	0.80	0.77	–0.44

If $E°_{Zn^{2+}/Zn} = -0.76\ V$, which cathode will give a maximum value of $E°_{cell}$ per electron transferred? **[2019, 11 Jan Shift-I]**

(a) $\frac{Ag^+}{Ag}$ (b) $\frac{Fe^{2+}}{Fe}$
(c) $\frac{Au^{3+}}{Au}$ (d) $\frac{Fe^{3+}}{Fe^{2+}}$

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Ans. ***(a)***

Cell Anode (A) Cathode (C)	$E^\circ_{cell}(SRP) = E^\circ_C - E^\circ_A$	E°_{cell} free electron transfer
1. $[Zn + 2Ag^+ \rightarrow \underset{Zn^{2+} + 2Ag}{\overset{Ag}{}}]$	$0.80 - (-0.76) = +1.56\ V$ for $2e^-$	$+\frac{1.56}{2} = +0.78\ V$
2. $[Zn + Fe^{2+} \rightarrow \underset{Zn^{2+} + Fe}{\overset{Fe}{}}]$	$-0.44 - (-0.76) = +0.32\ V$ for $2e^-$	$+\frac{0.32}{2} = +0.16\ V$
3. $[3Zn + 2Au^{3+} \rightarrow \underset{3Zn^{2+} + 2Au}{\overset{Au}{}}]$	$1.40 - (-0.76) = +2.4\ V$ for $6e^-$	$+\frac{2.16}{6} = +0.36\ V$
4. $[3Zn + 2Fe^{3+} \rightarrow \underset{3Zn^{2+} + 2Fe^{2+}}{\overset{Fe}{}}]$	$0.77 - (-0.76) = +1.53\ V$ for $2e^-$	$+\frac{1.53}{2} = +0.765\ V$

64 The standard electrode potential E° and its temperature coefficient $\left(\frac{dE^\circ}{dT}\right)$ for a cell are 2V and $-5\times10^{-4}\ VK^{-1}$ at 300 K respectively. The cell reaction is $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The standard reaction enthalpy ($\Delta_r H^\ominus$) at 300 K in kJ mol^{-1} is,
[Use, $R = 8\ JK^{-1}\ mol^{-1}$ and $F = 96{,}000\ C\ mol^{-1}$]

(a) −412.8 (b) −384.0
(c) 206.4 (d) 192.0

[2019, 12 Jan Shift-I]

Ans. ***(a)***

Given, $E^\circ = 2V, \left(\frac{dE^\circ}{dT}\right)$
$= -5\times10^{-4}\ VK^{-1}$
$T = 300\ K$
$R = 8\ JK^{-1}mol^{-1}$,
$F = 96000\ Cmol^{-1}$

According to Gibbs-Helmholtz equation,
$\Delta G = \Delta H - T\Delta S$ ...(i)
Also, $\Delta G = -nFE^\circ_{cell}$ ...(ii)
On substituting the given values in equation (ii), we get
$\Delta G = -2\times96000\ C\ mol^{-1}\times2\ V$
[$\because n = 2$ for the given reaction]
$= -4\times96000\ J\ mol^{-1}$
$= -384000\ J\ mol^{-1}$

Now, $\Delta S = nF\left(\frac{dE^\circ}{dT}\right)$
$\Delta S = 2\times96000\ C\ mol^{-1}\times(-5\times10^{-4}\ VK^{-1})$
$= -96\ JK^{-1}\ mol^{-1}$

Thus, on substituting the values of ΔG and ΔS in
Eq. (i), we get $-384000\ J\ mol^{-1}$
$= \Delta H - 300\ K\times(-96\ JK^{-1}mol^{-1})$
$\Delta H = -384000 - 28800\ J\ mol^{-1}$
$= -412800\ J\ mol^{-1}$
$= -412.800\ kJ\ mol^{-1}$

65 Given the equilibrium constant (K_C) of the reaction :
$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
is 10×10^{15}, calculate the E°_{cell} of this reaction at 298 K.
$\left[2.303\frac{RT}{F}\text{ at }298\ K = 0.059\ V\right]$

[2019, 11 Jan Shift-II]

(a) 0.4736 V (b) 0.04736 mV
(c) 0.4736 mV (d) 0.04736 V

Ans. ***(a)***

According to Nernst equation,
$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF}\log Q$$
Given, $\frac{2.303\ RT}{F} = 0.059\ V$
$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log Q$$
At equilibrium, $E_{cell} = 0$
$$E^\circ_{cell} = \frac{0.059}{n}\log K_C$$
For the given reaction,
$n = 2$
Also, $K_C = 10\times10^{15}$ [given]
$$\therefore \quad E^\circ_{cell} = \frac{0.059}{2}\log(10\times10^{15})$$
$= 0.472\ V \approx 0.473\ V$

66 Given, $E^\circ_{Cl_2/Cl^-} = 1.36\ V$,
$E^\circ_{Cr^{3+}/Cr} = -0.74\ V$
$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V$,
$E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\ V$

Among the following, the strongest reducing agent is

[JEE Main 2017]

(a) Cr (b) Mn^{2+} (c) Cr^{3+} (d) Cl^-

Ans. ***(a)***

The substances which have lower reduction potentials are stronger reducing agents. Therefore, Cr ($E^\circ_{Cr^{3+}/Cr} = -0.74\ V$) is the strongest reducing agent among all the other given options.

67 Given below are the half-cell reactions
$Mn^{2+} + 2e^- \longrightarrow Mn,\ E^\circ = -1.18\ V$
$2(Mn^{3+} + e^- \longrightarrow Mn^{2+}),$
$E^\circ = +1.51\ V$

The E° for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be **[JEE Main 2014]**

(a) −2.69V, the reaction will not occur
(b) −2.69 V the reaction will occur
(c) −0.33V, the reaction will not occur
(d) −0.33 V, the reaction will occur

Ans. ***(a)***

$Mn^{2+} + 2e^- \longrightarrow Mn,\ E^\circ = -1.18\ V$ ...(i)
$2(Mn^{3+} + e^- \longrightarrow Mn^{2+}),\ E^\circ = +1.51\ V$ ...(ii)
Subtracting Eq. (ii) from Eq. (i), we get
$3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$
$E^\circ = -1.18 - (+1.51) = -2.69\ V$

Since, the value of E° is –ve, therefore the reaction is non-spontaneous.

Alternate method
$Mn^{2+} + 2e^- \longrightarrow Mn,\ E^\circ = -1.18\ V$ ...(i)
$\Delta G^\circ = -nFE^\circ$ [here, n = number of e^- involved in the reaction]
$\Delta G_1^\circ = -2F(-1.18) = 2.36\ F$
$2Mn^{3+} + 2e^- \longrightarrow 2Mn^{2+},\ E^\circ = +1.51\ V$ ...(ii)
$\Delta G_2^\circ = -2F[1.51] = -3.02\ F$
Subtracting Eq. (ii) from Eq. (i), we get
$3Mn^{2+} \longrightarrow Mn + 2Mn^{3+},$ [$n = 2$]
$\Delta G_3^\circ = -2FE^\circ$
$\Delta G_3^0 = \Delta G_1^0 - \Delta G_2^0 = 5.38\ F$
$\Rightarrow \quad -2FE^\circ = 5.38\ F$
$\Rightarrow \quad E^\circ = -2.69\ V$

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68 Given, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V;

$E^\circ_{MnO_4^-/Mn^{2+}} = 1.51$ V

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V;

$E^\circ_{Cl/Cl^-} = 1.36$ V

Based on the data given above, strongest oxidising agent will be **[JEE Main 2013]**

(a) Cl (b) Cr^{3+}

(c) Mn^{2+} (d) MnO_4^-

Ans. ***(d)***

Higher the SRP (Standard Reduction Potential), stronger is the oxidising agent Among the given, electrode potentials, $E^\circ_{MnO_4^-/Mn^{2+}}$ is highest. Hence, MnO_4^- is the strongest oxidising agent.

69 The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are – 0.76, – 0.23 and – 0.44 V, respectively. The reaction $X + Y^{2+} \longrightarrow X^{2+} + Y$ will be spontaneous when **[AIEEE 2012]**

(a) $X = Ni, Y = Fe$ (b) $X = Ni, Y = Zn$

(c) $X = Fe, Y = Zn$ (d) $X = Zn, Y = Ni$

Ans. ***(d)***

A cell reaction is spontaneous, if $\Delta G^\circ < 0$.

Since, $\Delta G^\circ = -nFE^\circ_{cell}$

Thus, $E^\circ_{cell} > 0$, $E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$

$$\underset{\text{Oxi}}{X} + Y^{2+} \longrightarrow X^{2+} + \underset{\text{Red}}{Y}$$

(a) $X = Ni, \ Y = Fe$

$Ni + Fe^{2+} \longrightarrow Ni^{2+} + Fe$

$E^\circ_{Ni/Ni^{2+}} = +0.23$ V

$E^\circ_{Fe^{2+}/Fe} = -0.44$ V

Thus, $E^\circ_{cell} = E^\circ_{Ni/Ni^{2+}} + E^\circ_{Fe^{2+}/Fe}$

$= -0.21$ V

$E^\circ_{cell} < 0$

$\Rightarrow$ Reaction is non-spontaneous.

(b) $X = Ni, \ Y = Zn$

$Ni + Zn^{2+} \longrightarrow Ni^{2+} + Zn$

$E^\circ_{Ni/Ni^{2+}} = 0.23$ V

$E^\circ_{Zn^{2+}/Zn} = -0.76$ V

$\therefore \ E^\circ_{cell} = 0.23 + (-0.76) = -0.53$ V

$E^\circ_{cell} < 0$

$\Rightarrow$ Non-spontaneous reaction.

(c) $X = Fe, Y = Zn$

$Fe + Zn^{2+} \longrightarrow Fe^{2+} + Zn$

$E^\circ_{cell} = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Zn^{2+}/Zn}$

$= 0.44 - 0.76 = -0.32$ V

$E^\circ_{cell} < 0$

$\Rightarrow$ Non-spontaneous reaction.

(d) $X = Zn, \ Y = Ni$

$Zn + Ni^{2+} \longrightarrow Zn^{2+} + Ni$

$E^\circ_{cell} = E^\circ_{Zn/Zn^{2+}} + E^\circ_{Ni^{2+}/Ni}$

$= 0.76 - 0.23$

$= 0.53$ V

$E^\circ_{cell} > 0$

$\Rightarrow$ Spontaneous reaction.

70 In view of the signs of $\Delta_r G^\circ$ for the following reactions

$PbO_2 + Pb \longrightarrow 2PbO, \ \Delta_r G^\circ < 0$

$SnO_2 + Sn \longrightarrow 2SnO, \ \Delta_r G^\circ > 0$

Which oxidation states are more characteristic for lead and tin? **[AIEEE 2011]**

(a) For lead + 4, for tin + 2

(b) For lead + 2 , for tin + 2

(c) For lead + 4, for tin + 4

(d) For lead + 2, for tin + 4

Ans. ***(d)***

$$\underset{\text{Oxidation state}}{PbO_2} + \underset{0}{Pb} \longrightarrow \underset{+2}{2PbO}$$

Since, $\Delta G^\circ < 0$, *i.e.*, it is negative. Therefore, the reaction is spontaneous in the forward direction. This suggest that Pb^{2+} is more stable than Pb^{4+}.

$$\underset{\text{Oxidation state}}{SnO_2} + \underset{0}{Sn} \longrightarrow \underset{+2}{2SnO}$$

Since, $\Delta_r G^\circ > 0$, *i.e.*, it is positive, therefore, the reaction is non-spontaneous in the forward direction. But it will be spontaneous in the backward direction. This suggests that Sn^{4+} will be more stable than Sn^{2+}. These facts are also supported by the inert pair effect down the group.

71 The reduction potential of hydrogen half-cell will be negative if **[AIEEE 2011]**

(a) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M

(b) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M

(c) $p(H_2) = 2$ atm and $[H^+] = 1.0$ M

(d) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M

Ans. ***(c)***

For hydrogen electrode,

$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$

$$E = E^\circ - \frac{0.0591}{n}\log\frac{(p_{H_2})^{1/2}}{[H^+]}$$

Here, n = number of electrons involved in the reaction

$$E = E^\circ - \frac{0.0591}{1}\log\frac{(pH_2)^{1/2}}{[H^+]}$$

$$E = -0.0591\log\frac{(p_{H_2})^{1/2}}{[H^+]}$$

$[\because E^\circ = 0$ for H– electrode$]$

$\Rightarrow E$ will be –ve when $\frac{(p_{H_2})^{1/2}}{[H^+]}$ is +ve.

i.e., $(p_{H_2})^{1/2} > [H^+]$

	p_{H_2}	$[H^+]$	$\frac{(pH_2)^{1/2}}{[H^+]}$	E_{red}
(a)	1 atm	2.0 M	0.25	+ve
(b)	1 atm	1.0 M	1.0	0
(c)	2 atm	1.0 M	2.0	–ve
(d)	2 atm	2.0 M	0.50	+ ve

Hence, when $p(H_2)$ is 2 atm and $[H^+]$ is 1.0 M, E_{red} is negative.

72 The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows **[AIEEE 2010]**

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2,$$

$\Delta_r G = +966$ kJ mol^{-1}

The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least

(a) 4.5 V (b) 3.0 V

(c) 2.5 V (d) 5.0 V

Ans. ***(c)***

$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2$

Thus, $\frac{2}{3} \times 3(O^{2-})$

i.e., $2O^{2-} \longrightarrow O_2 + 4e^{-1}$ $[\because n = 4]$

$\Delta G = +966$ kJ mol^{-1}

$= 966 \times 10^3$ J mol^{-1}

$\Delta G = -nFE_{cell}$

$966 \times 10^3 = -4 \times 96500 \times E_{cell}$

$\Rightarrow \ E_{cell} = 2.5$ V

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73 Given, $E^\circ_{Fe^{3+}/Fe} = -0.036$ V,

$E^\circ_{Fe^{2+}/Fe} = -0.439$ V

The value of standard electrode potential for the charge,

[AIEEE 2009]

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$

will be

(a) - 0.072 V (b) 0.385 V

(c) 0.770 V (d) - 0.270 V

Ans. ***(c)***

It is given that,

$Fe^{3+} + 3e^- \longrightarrow Fe$, $E_1^\circ = -0.036$ V ...(i)

$Fe^{2+} + 2e^- \longrightarrow Fe$, $E_2^\circ = -0.439$ V ...(ii)

We need to calculate

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$, $E_3^\circ = ?$ ...(iii)

Equation (iii) can be obtained by subtacting Eq. (ii) from (i) but E_0 being an intensive property, cannot be calculated by this way. In order to calculate E_3°, concept of ΔG° is used .

ΔG_1° for Eq. (i) is given by

$\Delta G_1^\circ = -3 \times F \times (-0.036)$

$\Rightarrow \Delta G_1^\circ = +0.108F$

ΔG_2° for Eq. (ii) is given by

$\Delta G_2^\circ = -2 \times F \times (-0.439)$

$\Rightarrow \Delta G_2^\circ = 0.878F$

ΔG_3° for Eq. (iii) is given by

$\Delta G_3^\circ = -1 \times F \times E_3^\circ \Rightarrow \Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$

$\Rightarrow -1 \times F \times E_3^\circ = 0.108F - 0.878F$

$\Rightarrow E_3^\circ = 0.770$V

74 Given, $E^\circ_{Cr^{3+}/Cr} = 0.72$ V,

$E^\circ_{Fe^{2+}/Fe} = -0.42$ V.

The potential for the cell

$Cr|Cr^{3+}(0.1M)||Fe^{2+}(0.01M)|Fe$ is

[AIEEE 2008]

(a) 0.26 V (b) 0.399 V

(c) - 0.339 V (d) - 0.26 V

Ans. ***(a)***

$Cr|Cr^{3+}(0.1\,M)||Fe^{2+}(0.01\,M)|Fe$

Oxidation half cell

$Cr \longrightarrow Cr^{3+} + 3e^- \times 2$

Reduction half cell

$Fe^{2+} + 2e^- \longrightarrow Fe \times 3$

Net cell reaction

$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$; $n = 6$

$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$

$= 0.72 - 0.42 = 0.30$V

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$

$= 0.30 - \frac{0.0591}{6} \log \frac{(0.1)^2}{(0.01)^3}$

$= 0.30 - \frac{0.0591}{6} \log \frac{10^{-2}}{10^{-6}}$

$= 0.30 - \frac{0.0591}{6} \log 10^4$

$E_{cell} = 0.2606$ V

75 The cell, $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$ ($E^\circ_{cell} = 1.10$ V), was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is

[AIEEE 2007]

(a) antilog (24.08) (b) 37.3

(c) $10^{37.3}$ (d) 9.65×10^4

Ans. ***(c)***

Cell is completely discharged. It means equilibrium gets established, $E_{cell} = 0$

$Zn|Zn^{2+}(1\,M)||Cu^{2+}(1\,M)|Cu$

Cell reaction : $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

We know, $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log K_{eq}$

$E^\circ_{cell} = \frac{0.0591}{n} \log K_{eq}$

or $1.10 = \frac{0.0591}{2} \log K_{eq}$

$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$= \text{antilog} \frac{2.20}{0.0591} = \text{antilog}\, 37.3$

76 Given the data at 25°C,

$Ag + I^- \longrightarrow AgI + e^-$; $E^\circ = 0.152$ V

$Ag \longrightarrow Ag^+ + e^-$; $E^\circ = -0.8$ V

What is the value of $\log K_{sp}$ for AgI ?

$\left(2.303 \frac{RT}{F} = 0.059 \text{ V}\right)$ **[AIEEE 2006]**

(a) – 8.12 (b) + 8.612

(c) –37.83 (d) –16.13

Ans. ***(d)***

$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$; $E_1^\circ = -0.152$

$Ag(s) \longrightarrow Ag^+ + e^-$; $E_2^\circ = -0.8$

$AgI(s) \longrightarrow Ag^+ + I^-$; $E^\circ = -0.952$ $[E^\circ = E_1^\circ + E_2^\circ]$

$E^\circ_{cell} = \frac{0.059}{n} \log K_{sp}$

$-0.952 = \frac{0.059}{1} \log K_{sp}$

$\log K_{sp} = \frac{-0.952}{0.059} = -16.135$

77 The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are – 0.41, + 1.57, + 0.77 and + 1.97 V, respectively. For which one of these metals, the change in oxidation state from + 2 to + 3 is easiest ? **[AIEEE 2004]**

(a) Cr (b) Mn

(c) Fe (d) Co

Ans. ***(a)***

$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41$ V

$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.57$ V

$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77$ V

$E^\circ_{Co^{3+}/Co^{2+}} = +1.97$ V

More negative value of E°_{red} indicates better reducing agent. Thus, easily oxidised. Hence, oxidation of Cr^{2+} to Cr^{3+} is the easiest.

78 Consider the following E° values :

$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77$ V

$E^\circ_{Sn^{2+}/Sn} = -0.14$ V

Under standard conditions, the potential for the reaction

$Sn(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$ is **[AIEEE 2004]**

(a) 1.68 V (b) 1.40 V

(c) 0.91 V (d) 0.63 V

Ans. ***(c)***

$Sn(s) + 2Fe^{3+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$

$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$

$= E^\circ_{Sn/Sn^{2+}} + E^\circ_{Fe^{3+}/Fe^{2+}}$

Given, $E^\circ_{Sn^{2+}/Sn} = -0.14$ V

$\therefore E^\circ_{Sn/Sn^{2+}} = +0.14$ V

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V

$\therefore E^\circ_{cell} = 0.14 + 0.77 = 0.91$ V

79 In a cell that utilises the reaction

$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

addition of H_2SO_4 to cathode compartment will **[AIEEE 2004]**

(a) lower the E and shift equilibrium to the left

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(b) lower the E and shift the equilibrium to the right
(c) increase the E and shift the equilibrium to the right
(d) increase the E and shift the equilibrium to the left

Ans. ***(c)***

$Zn(s) + 2H^+ \longrightarrow Zn^{2+}(aq) + H_2(g)$

Reaction quotient, $Q = \dfrac{[Zn^{2+}]}{[H^+]^2}$

Corresponding cell is

$$\underset{\text{Anode}}{Zn\,|\,Zn^{2+}(C_1)} \;||\; H^+(aq)\,|\,\underset{\text{Cathode}}{Pt(H_2)}$$

and $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{2}\log K$

$$= E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[H^+]^2}$$

$$= E^\circ_{cell} + \frac{0.0591}{2}\log\frac{[H^+]^2}{[Zn^{2+}]}$$

If H_2SO_4 is added to cathodic compartment, (towards reactant side), then Q decrease (due to increase in H^+).

Hence, equilibrium is displaced towards right and E_{cell} increases.

80 The standard emf of a cell, involving one electron change is found to be 0.591 V at 25° C. The equilibrium constant of the reaction is (F = 96500 C mol^{-1}) **[AIEEE 2004]**

(a) 1.0×10^1 (b) 1.0×10^5
(c) 1.0×10^{10} (d) 1.0×10^{30}

Ans. ***(c)***

Relation between K_{eq} and E°_{cell} is

$$E^\circ_{cell} = \frac{2.303\,RT}{nF}\log K_{eq}$$

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_{eq}\ (\text{at } 298\ K)$$

$$0.591 = \frac{0.0591}{1}\log K_{eq}$$

$\therefore \quad \log K_{eq} = 10$

$\Rightarrow \quad K_{eq} = 1 \times 10^{10}$

81 Standard reduction electrode potentials of three metals A, B and C are + 0.5 V, – 3.0 V and – 1.2 V, respectively. The reducing power of these metals are **[AIEEE 2003]**

(a) $B > C > A$
(b) $A > B > C$
(c) $C > B > A$
(d) $A > C > B$

Ans. ***(a)***

More negative value of E° means higher reducing power.

82 For the redox reaction

$Zn(s) + Cu^{2+}(0.1\ M) \longrightarrow Zn^{2+}(1\ M) + Cu(s)$

taking place in a cell, E°_{cell} is 1.10 V.

E_{cell} for the cell will be

$\left(2.303\dfrac{RT}{F} = 0.0591\right)$ **[AIEEE 2003]**

(a) 2.14 V (b) 1.80 V
(c) 1.07 V (d) 0.82 V

Ans. ***(c)***

By using Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log Q$$

$$\underset{0.1\,M}{Cu^{2+}} + Zn \longrightarrow \underset{1M}{Zn^{2+}} + Cu$$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{0.1} = 10$$

$$E_{cell} = 1.10 - \frac{0.0591}{2}\log 10$$

$$= 1.10 - 0.0295$$

$$= 1.0705\ V$$

83 For a cell reaction involving a two electron change, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be **[AIEEE 2003]**

(a) 1×10^{-10} (b) 29.5×10^{-2}
(c) 10 (d) 1×10^{10}

Ans. ***(d)***

The standard emf of the cell,

$$E^\circ_{cell} = \frac{2.303\,RT}{nF}\log K_{eq}$$

$$\Rightarrow \quad 0.295 = \frac{0.0591}{2}\log K_{eq}$$

$\therefore \quad \log K_{eq} = 10 \Rightarrow K_{eq} = 1 \times 10^{10}$

84 Which of the following reaction is possible at anode ? **[AIEEE 2002]**

(a) $Fe_2 + 2e^- \longrightarrow 2F^-$

(b) $2H^+ + \dfrac{1}{2}O_2 + 2e^- \longrightarrow H_2O$

(c) $2Cr_2^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$

(d) None of the above

Ans. ***(c)***

Oxidation takes place at anode. Hence, (a), (b) is not feasible as these are reduction reactions. But Cr^{3+} is oxidised to $Cr^{6+}(Cr_2O_7^{2-})$ under given condition.

85 For a cell given below

$Ag\,|\,Ag^+\,||\,Cu^{2+}\,|\,Cu$

$Ag^+ + e^- \longrightarrow Ag;\ E^\circ = x$

$Cu^{2+} + 2e^- \longrightarrow Cu;\ E^\circ = y$

E° cell is **[AIEEE 2002]**

(a) $x + 2y$
(b) $2x + y$
(c) $y - x$
(d) $y - 2x$

Ans. ***(c)***

At LHS (oxidation)

$2 \times (Ag \longrightarrow Ag^+ + e^-);\quad E^\circ_{oxi} = -x$

At RHS (reduction)

$Cu^{2+} + 2e^- \longrightarrow Cu \qquad E^\circ_{red} = +y$

$2Ag + Cu^{2+} \longrightarrow Cu + 2Ag^+,$

$E^\circ_{red} = (y - x)$

Note E° values remain constant when half-cell equation is multiplied/divided.

86 For the following cell with hydrogen electrodes at two different pressures p_1 and p_2

$$\underset{p_1}{Pt(H_2)}\,|\,\underset{1M}{H^+(aq)}\,|\,\underset{p_2}{Pt(H_2)}$$

emf is given by **[AIEEE 2002]**

(a) $\dfrac{RT}{F}\log_e\dfrac{p_1}{p_2}$ (b) $\dfrac{RT}{2F}\log_e\dfrac{p_1}{p_2}$

(c) $\dfrac{RT}{F}\log_e\dfrac{p_2}{p_1}$ (d) $\dfrac{RT}{2F}\log_e\dfrac{p_2}{p_1}$

Ans. ***(b)***

LHS half cell

$$\underset{p_1}{H_2(g)} \longrightarrow 2H^+(1\ M) + 2e^-$$

RHS half cell

$$2H^+(1\ M) + 2e^- \longrightarrow \underset{p_2}{H_2(g)}$$

$$\underset{p_1}{H_2(g)} \longrightarrow \underset{p_2}{H_2(g)}$$

$E^\circ_{cell} = 0.00\ V,$

$K = \dfrac{p_2}{p_1},\ n = 2$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\log_e K$$

$$= 0 - \frac{RT}{2F}\log_e\frac{p_2}{p_1}$$

$$E_{cell} = \frac{RT}{2F}\log_e\frac{p_1}{p_2}$$

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TOPIC 3
Batteries, Fuel Cells and Corrosion

87 Compound *A* used as a strong oxidising agent is amphoteric in nature. It is the part of lead storage batteries. Compound *A* is
[2021, 26 Feb Shift-I]

(a) PbO_2 (b) PbO
(c) $PbSO_4$ (d) Pb_3O_4

Ans. ***(a)***

In the set of four lead compounds Pb (II) compounds are PbO and $PbSO_4$. PbO_2 is a Pb (IV) compound whereas Pb_3O_4 is a mixed oxide of Pb (II) and Pb (IV) i.e. $2\overset{II}{P}b\overset{(IV)}{O}\cdot\overset{(IV)}{P}bO_2$.

Pb is a member of group 14 and it shows +2 and +4 oxidation states. But due to inert pair effect, Pb^{2+} is more stable than Pb^{4+}. So, Pb (IV) compounds are strong oxidising agents as Pb^{4+} gets easily reduced to more stable Pb^{2+}.

$Pb^{+4} + 2e^- \longrightarrow Pb^{2+}, \Delta G° < 0$ (spontaneous)

So, PbO_2 or Pb_3O_4 can be the compound *A*. But out of these two compounds only PbO_2 is used in lead storage batteries where a grid of lead packed with PbO_2 acts as cathode and also it is amphoteric in nature. It reacts with both acids and alkali.

(i) $\overset{+4}{P}bO_2 + 2\overset{-1}{H}Cl \longrightarrow \overset{+2}{P}bCl_2 + \overset{0}{Cl_2} + H_2O$

Here, PbO_2 acts as a basic oxide as well as an oxidising agent.

(ii) $PbO_2 + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$

Here, PbO_2 acts as an acidic oxide.

So, the compound *A* is PbO_2 (option-a).

88 The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolysed in g during the process is (Molar mass of $PbSO_4 = 303 g\ mol^{-1}$)
[2019, 9 Jan Shift-I]

(a) 11.4 (b) 7.6
(c) 15.2 (d) 22.8

Ans. ***(b)***

Key Idea This question is based upon Faraday's first law which states that "Mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed."

During charging :

$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

$\Rightarrow$ $1\ F \equiv 1$ g-equiv. of $PbSO_4$

$= \frac{1}{2}$ mol of $PbSO_4$

$\Rightarrow$ $\frac{303}{2}$ g $PbSO_4$

$\therefore$ $0.05\ F \equiv \frac{303}{2} \times 0.05$ g of $PbSO_4$

$= 7.575$ g of $PbSO_4$

89 Galvanisation is applying a coating of
[JEE Main 2016]

(a) Cr (b) Cu
(c) Zn (d) Pb

Ans. ***(b)***

Zinc metal is the most stable metal to cover iron surfaces. The process of coating the iron surface by zinc is called galvanisation.

90 In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is

$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are –166.2, –237.2 and –394.4 kJ mol^{-1}, respectively. If standard enthalpy of combustion of methanol is –726 kJ mol^{-1}, efficiency of the fuel cell will be
[AIEEE 2009]

(a) 80% (b) 87%
(c) 90% (d) 97%

Ans. ***(d)***

Percentage efficiency of the fuel cell

$= \frac{\Delta G}{\Delta H} \times 100$

The concerned reaction is

$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta G_r = [\Delta G_f(CO_2, g) + 2\Delta G_f(H_2O, l)]$
$[-\Delta G_f(CH_3OH, l) - \frac{3}{2}\Delta G_f(O_2, g)]$

$= -394.4 + 2(-237.2) - (-166.2) - 0$
$= -394.4 - 474.4 + 166.2$
$= -702.6$ kJ mol^{-1}

Percentage efficiency

$= \frac{702.6}{726} \times 100$

$= 96.78\% \approx 97\%$

91 In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to
[AIEEE 2004]

(a) generate heat
(b) create potential difference between the two electrodes
(c) produce high purity water
(d) remove adsorbed oxygen from electrode surfaces

Ans. ***(b)***

Any cell (like fuel cell), works when potential difference is developed.

92 Several blocks of magnesium are fixed to the bottom of a ship to
[AIEEE 2003]

(a) keep away the sharks
(b) make the ship lighter
(c) prevent action of water and salt
(d) prevent puncturing by under sea rocks

Ans. ***(c)***

Magnesium usually have a thin layer of MgO over its surface which prevents the underneath of metal from reacting with moisture. Thus, several blocks of magnesium are fixed to the bottom of a ship to prevent action of water and salt.

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11

Chemical Kinetics

TOPIC 1

Rate of Chemical Reaction and Rate Expression

01 The reaction that occurs in a breath analyser, a device used to determine the alcohol level in a person's blood stream is

$$2K_2Cr_2O_7 + 8H_2SO_4 + 3C_2H_6O \rightarrow 2Cr_2(SO_4)_3 + 3C_2H_4O_2 + 2K_2SO_4 + 11H_2O$$

If the rate of appearance of $Cr_2(SO_4)_3$ is 2.67 mol min^{-1} at a particular time, the rate of disappearance of C_2H_6O at the same time is ..... mol min^{-1}. (Nearest integer)

[2021, 27 Aug Shift-I]

Ans. ***(4)***

Rate of appearence of 2 moles of $Cr_2(SO_4)_3$,

$$\frac{d}{dt}[Cr_2(SO_4)_3] = 2.67 \text{ mol/min}$$

Rate of disappearence of 3 moles of C_2H_6O, $\frac{d[C_2H_6O]}{dt}$

$$= \frac{3}{2}\frac{d[Cr_2(SO_4)_3]}{dt} = \frac{2.67}{2} \times 3$$

$$= 4.005$$

$$= 4 \text{ mol/min}$$

02 The reaction rate for the reaction

$$[PtCl_4]^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3]^- + Cl^-$$

was measured as a function of concentrations of different species. It was observed that

$$\frac{-d[(PtCl_4)^{2-}]}{dt}$$

$$= 4.8 \times 10^{-5}[(PtCl_4)^{2-}]$$

$$= 2.4 \times 10^{-3}[\{Pt(H_2O)Cl_3\}^-][Cl^-]$$

where, square brackets are used to denote molar concentrations. The equilibrium constant, K_C = ... (Nearest integer)

[2021, 26 Aug Shift-II]

Ans. ***(50)***

Consider, at equilibrium $\frac{d[(PtCl_4)^{2-}]}{dt} = 0$

$$\therefore 4.8 \times 10^{-5}[(PtCl_4)^{2-}] = 2.4 \times 10^{-3}[\{Pt(H_2O)Cl_3\}^-][Cl^-]$$

Equilibrium constant,

$$K_C = \frac{[PtCl_4]^{2-}}{[Pt(H_2O)Cl_3]^-[Cl^-]}$$

$$= \frac{2.4 \times 10^{-3}}{4.8 \times 10^{-5}} = 0.50 \times 100 = 50$$

03 For a chemical reaction $A \longrightarrow B$, it was found that concentration of B is increased by 0.2 mol L^{-1} in 30 min. The average rate of the reaction is .....$\times 10^{-1}$ mol L^{-1} h^{-1}. (Nearest integer)

[2021, 25 July Shift-II]

Ans. ***(4)***

Reaction, $A \longrightarrow B$

At $t = 0$ 0

At $t = 30$ min 0.2 M

Here, initially at time zero, reaction is constant but after 30 minutes concentration of B is increased by 0.2 mol L^{-1}.

$$\text{Average rate of reaction} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} = \frac{(0.2-0)}{\frac{1}{2}}$$

$$= 0.4 \text{ mol } L^{-1} h^{-1}$$

$$= 4 \times 10^{-1} \text{ mol } L^{-1} h^{-1}$$

04 $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

In the above first order reaction, the concentration of PCl_5 reduces from initial concentration 50 mol L^{-1} to 10 mol L^{-1} in 120 minutes at 300 K. The rate constant for the reaction at 300 K is $x \times 10^{-2}$ min^{-1}. The value of x is ..... . [Given, log 5 = 0.6989]

[2021, 20 July Shift-II]

Ans. ***(1)***

$$PCl_5(g) \xrightarrow{300K} PCl_3(g) + Cl_2(g)$$

It is of first order reaction.

$t = 0$ 50 M

$t = 120$ min 10 M

For first order reaction,

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A_t]}$$

$[A_0]$ = Initial concentration of PCl_5

$[A_t]$ = Concentration of PCl_5 at $t = 120$ min.

$$k = \frac{2.303}{120}\log\frac{50}{10}$$

$$= \frac{2.303}{120} \times 0.6989$$

$$= 0.013413 \text{ min}^{-1}$$

$$= 1.3413 \times 10^{-2} \text{ min}^{-1}$$

1.34 = Nearest integer = 1

05 The reaction $2A + B_2 \longrightarrow 2AB$ is an elementary reaction. For a certain quantity of reactants, if the volume of the reaction vessel is reduced by a factor of 3, the rate of the reaction increases by a factor of ..... . (Round off to the nearest integer).

[2021, 17 March Shift-II]

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Ans. ***(27)***

Given, the reaction $2A + B_2 \longrightarrow 2AB$ is an elementary reaction.

So, rate of reaction $= k[A]^2[B_2]$

Initial rate $= k(a/V)^2(b/V)^1$

where, a and b are the number of moles of A and B and V is the volume.

On reducing the volume by a factor of 3, the concentrations of A and B_2 will become 3 times

Final rate $= k(3a/V)^2(3b/V)^1$

$3^2 \times 3k\left(\frac{a}{V}\right)^2\left(\frac{b}{V}\right)^1 = 27 \times$ initial rate

Hence, the rate becomes $3^2 \times 3 = 27$ times of initial rate.

06 For the reaction $2A + 3B + \frac{3}{2}C \rightarrow 3P$, which statement is correct?

[2020, 3 Sep Shift-II]

(a) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

(b) $\frac{dn_A}{dt} = \frac{3}{2}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

(c) $\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt}$

(d) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$

Ans. ***(d)***

For a reaction,

$$2A + 3B + \frac{3}{2}C \longrightarrow 3P$$

For a reaction, $aA + bB = cC$

Rate of reaction,

$$\Rightarrow \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt}$$

$\therefore$ For given reaction,

$$\frac{-1}{2}\frac{d[A]}{dt} = \frac{-1}{3}\frac{d[B]}{dt} = \frac{-2}{3}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[P]}{dt}$$

$$\frac{d[A]}{dt} = \frac{2}{3}\frac{d[B]}{dt} = \frac{4}{3}\frac{d[C]}{dt} = \frac{2}{3}\frac{d[P]}{dt}$$

07 For the reaction $2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$ the observed rate expression is, rate $= K_f[NO]^2[H_2]$. The rate expression for the reverse reaction is **[2020, 7 Jan Shift-II]**

(a) $K_b[N_2][H_2O]^2/[H_2]$

(b) $K_b[N_2][H_2O]$

(c) $K_b[N_2][H_2O]^2/[NO]$

(d) $K_b[N_2][H_2O]^2$

Ans. ***(a)***

$$2H_2(g) + 2NO(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

Rate law for forward reaction is given as:

$$\text{rate} = K_f[NO]^2[H_2]$$

Rate of forward reaction is equal to rate of reverse reaction at equilibrium and also,

at equilibrium $(K) = \frac{K_f}{K_b}$

where, K (equilibrium constant)

$$= \frac{[N_2][H_2O]^2}{[H_2]^2[NO]^2} \Rightarrow \frac{K_f}{K_b} = \frac{[N_2][H_2O]^2}{[H_2]^2[NO]^2}$$

Rearranging :

$$K_f[H_2][NO]^2 = K_b[N_2][H_2O]^2/[H_2]$$

$\therefore$ Rate of reverse reaction

$$= K_b[N_2][H_2O]^2/[H_2]$$

08 NO_2 required for a reaction is produced by the decomposition of N_2O_5 in CCl_4 as per the equation, $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ he initial concentration of N_2O_5 is 3.00 mol L^{-1} and it is 2.75 mol L^{-1} after 30 minutes. The rate of formation of NO_2 is

[2019, 12 April Shift-II]

(a) 4.167×10^{-3} mol L^{-1} min^{-1}

(b) 1.667×10^{-2} mol L^{-1} min^{-1}

(c) 8.333×10^{-3} mol L^{-1} min^{-1}

(d) 2.083×10^{-3} mol L^{-1} min^{-1}

Ans. ***(b)***

Key Idea The rate of a chemical reaction means the speed with which the reaction takes place.

For $R \longrightarrow P$

Rate of disappearance of R

$$= \frac{\text{Decrease in conc. of } R}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t}$$

Rate of appearance of P

$$= \frac{\text{Increase in conc. of } P}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t}$$

Given, $[N_2O_5]_{\text{initial}} = 3.00$ mol L^{-1}

After 30 min, $[N_2O_5] = 2.75$ mol L^{-1}

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$t = 0$ 3.0 M

$t = 30$ 2.75 M

From the equation, it can be concluded that

$$\frac{1}{2} \times \frac{-\Delta[N_2O_5]}{\Delta t} = \frac{1}{4} \times \frac{\Delta[NO_2]}{\Delta t}$$

$$= \frac{-\Delta[N_2O_5]}{\Delta t} = \frac{-(2.75 - 3.00)\text{ mol } L^{-1}}{30}$$

$$\Rightarrow \frac{0.25}{30}$$

and $\frac{\Delta[NO_2]}{\Delta t} = -2\frac{\Delta(N_2O_5)}{\Delta t}$

$$\Rightarrow \frac{\Delta[NO_2]}{\Delta t} = -2 \times \frac{0.25}{30}$$

$$= -1.667 \times 10^{-2} \text{ mol } L^{-1} \text{ min}^{-1}$$

09 In the following reaction; $xA \rightarrow yB$

$$\log_{10}\left[-\frac{d[A]}{dt}\right] = \log_{10}\left[\frac{d[B]}{dt}\right] + 0.3010$$

A and B respectively can be

[2019, 12 April Shift-I]

(a) n-butane and iso-butane

(b) C_2H_2 and C_6H_6

(c) C_2H_4 and C_4H_8

(d) N_2O_4 and NO_2

Ans. ***(c)***

In the given reaction; $x\,A \longrightarrow y\,B$

$$\log_{10}\left[\frac{-d[A]}{dt}\right] = \log_{10}\left[\frac{d[B]}{dt}\right] + 0.3010$$

Value of $\log 2 = 0.3010$

Substituting 0.3010 by $\log 2$

$$\log_{10}\left[-\frac{d[A]}{dt}\right] = \log_{10}\left[\frac{d[B]}{dt}\right] + \log 2$$

Using logarithm rules,

$$\left[\frac{-d[A]}{dt}\right] = 2 \times \left[\frac{d[B]}{dt}\right]$$

$$\Rightarrow -\frac{1}{2}\left[\frac{d[A]}{dt}\right] = \left[\frac{d[B]}{dt}\right] \quad \ldots(i)$$

Using the rate equation (i) to determine the reaction involved is

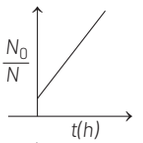
$$2A \longrightarrow B$$

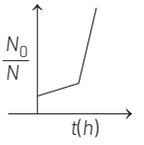
Option that fits correct in the above reaction is (c).

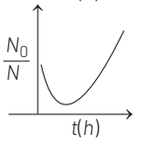
$$2C_2H_4 \longrightarrow C_4H_8.$$

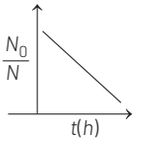
10 A bacterial infection in an internal wound grows as $N'(t) = N_0 \exp(t)$, where the time t is in hours. A dose of antibiotic, taken orally, needs 1 hour to reach the wound. Once it reaches there, the bacterial population goes down as $\frac{dN}{dt} = -5N^2$. What will be the plot of $\frac{N_0}{N}$ vs t after 1 hour ?

[2019, 10 April Shift-I]

(a) 

(b) 

(c) 

(d) 

Ans. ***(a)***

The expression for bacterial growth is

$$N = N_0 e^t$$

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$\Rightarrow \quad \frac{N_0}{N} = e^{-t}$

From 0 to 1 hour $N'(t) = N_0 e^t$

From 1 hour onwards, $\frac{dN}{dt} = -5N^2$

On differentiating the above equation from N' to N we get.

$$\int_{eN_0}^{N} N^{-2} dN = -5\int_{1}^{t} dt$$

$[\because$ At 1 hour, $N' = eN_0]$

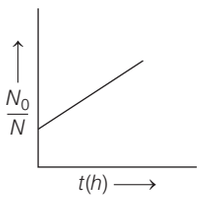
$$\left[\frac{1}{N} - \frac{1}{eN_0}\right] = 5(t-1)$$

Multiply both sides by N_0, we get

$$\frac{N_0}{N} - \frac{1}{e} = 5N_0(t-1)$$

or, $$\frac{N_0}{N} = 5N_0(t-1) + \frac{1}{e}$$

$$\frac{N_0}{N} = 5N_0 t + \left[\frac{1}{e} - 5N_0\right]$$



On comparing the above equation with equation of straight line, $y = mx + c$

We get $m = 5N_0$

$$c = \frac{1}{e} - 5N_0$$

$\therefore$ Plot of $\frac{N_0}{N}$ vs t is shown aside.

11 For a reaction scheme, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, if the rate of formation of B is set to be zero then the concentration of B is given by **[2019, 8 April Shift-II]**

(a) $k_1 k_2 [A]$ (b) $\left(\frac{k_1}{k_2}\right)[A]$

(c) $(k_1 - k_2)[A]$ (d) $(k_1 + k_2)[A]$

Ans. ***(b)***

$A \xrightarrow{K_1} B \xrightarrow{K_2} C$

Rate of formation of B is

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\Rightarrow \quad 0 = k_1[A] - k_2[B] \qquad \left[\because \text{Given}, \frac{d[B]}{dt} = 0\right]$$

$$\Rightarrow \quad k_2[B] = k_1[A]$$

$\Rightarrow$ Concentration of B, $[B] = \frac{k_1}{k_2}[A]$

12 For an elementary chemical reaction, $A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is **[2019, 10 Jan Shift-II]**

(a) $2k_1[A_2] - k_{-1}[A]^2$

(b) $k_1[A_2] - k_{-1}[A]^2$

(c) $2k_1[A_2] - 2k_{-1}[A]^2$

(d) $k_1[A_2] + k_{-1}[A]^2$

Ans.*(c)*

The elementary reaction, $A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$

follows opposing or reversible kinetics,

(i) Rate of the reaction,

$$r = r_{\text{forward}} - r_{\text{backward}}$$
$$= k_1[A_2] - k_{-1}[A]^2 \qquad \ldots(i)$$

(ii) Again, rate of the reaction can be expressed as,

$$r = -\frac{d[A_2]}{dt} = +\frac{1}{2}\frac{d[A]}{dt}$$

So, the rate of appearance of A,

i.e. $$\frac{d[A]}{dt} = 2r = 2k_1[A_2] - 2k_{-1}[A]^2$$

[From Eq. (i)]

13 Consider the reaction,

$$Cl_2(aq) + H_2S(aq) \longrightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is,

$$\text{rate} = k[Cl_2][H_2S]$$

Which of these mechanisms is/are consistent with this rate equation? **[AIEEE 2010]**

(I) $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)

$Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)

(II) $H_2S \rightleftharpoons H^+ + HS^-$ (fast)

$Cl_2 + HS^- \longrightarrow 2\,Cl^- + H^+ + S$ (slow)

(a) (II) only (b) Both (I) and (II)

(c) Neither (I) nor (II)

(d) (I) only

Ans. ***(d)***

Slowest step is the rate determining step. Thus, in case (I), rate law is given as rate $= k[Cl_2][H_2S]$

While for the reaction given in case (II), rate law is given as rate $= k[H_2S][Cl_2][H^+]^{-1}$.

Hence, only mechanism (I) is consistent with the given rate law.

14 For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression **[AIEEE 2008]**

(a) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

(b) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$

(c) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$

(d) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$

Ans. ***(b)***

$$\frac{1}{2}A \longrightarrow 2B$$

Remember for $aA \longrightarrow bB$

$$-\frac{1}{a}\frac{d[A]}{dt} = \frac{1}{b}\frac{d[B]}{dt} = \text{Rate of reaction}$$

For the given reaction

$$-\frac{2d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$$

$$= \text{Rate of reaction}$$

Rate of disappearance of $A = -\frac{d[A]}{dt}$

$$= \frac{1}{2\times 2}\frac{d[B]}{dt}$$

$$= \frac{1}{4}\frac{d[B]}{dt}$$

15 The rate equation for the reaction $2A + B \rightarrow C$ is found to be rate $= k\,[A]\,[B]$

The correct statement in relation to this reaction is that the **[AIEEE 2004]**

(a) unit of k must be s^{-1}

(b) $t_{1/2}$ is a constant

(c) rate of formation of C is twice the rate of disappearance of A

(d) value of k is independent of the initial concentrations of A and B

Ans. ***(d)***

$$2A + B \longrightarrow C$$

Rate $= k[A][B]$

It represents second order reaction.

Thus, unit of k is L mol^{-1} s^{-1}.

Hence, (a) is false.

$t_{1/2}$ is dependent of concentration but not constant. Hence, (b) is false.

And $$-\frac{1}{2}\frac{d[A]}{dt} = \frac{d[C]}{dt}$$

Thus, (c) is also false.

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16 For the reaction, $H_2 + I_2 \longrightarrow 2HI$, the differential rate law is **[AIEEE 2002]**

(a) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = 2\frac{d[HI]}{dt}$

(b) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

(c) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

(d) $-\frac{d[H_2]}{2dt} = -\frac{d[I_2]}{2dt} = \frac{d[HI]}{dt}$

Ans. ***(b)***

$$H_2 + I_2 \longrightarrow 2HI$$

Rate of reaction

$$= \frac{-d[H_2]}{dt} = \frac{-d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$$

or $\frac{-2d[H_2]}{dt} = \frac{-2d[I_2]}{dt} = \frac{d[HI]}{dt}$

17 Consider following two reactions,

$A \longrightarrow$ Product; $-\frac{d[A]}{dt} = k_1[A]^0$

$B \longrightarrow$ Product; $-\frac{d[B]}{dt} = k_2[B]$

k_1 and k_2 are expressed in terms of molarity (mol L^{-1}) and time (s^{-1}) as **[AIEEE 2002]**

(a) s^{-1}, M s^{-1} L^{-1} (b) M s^{-1}, M s^{-1}

(c) s^{-1}, M^{-1} s^{-1} (d) M s^{-1}, s^{-1}

Ans. ***(d)***

Unit of rate constant,

$$k = \frac{1}{\text{Time}} \cdot \frac{1}{(\text{conc})^{n-1}}$$

For k_1, $n = 0$, $k = \frac{1}{t} \cdot \frac{1}{(\text{conc})^{0-1}}$

Hence, conc $t^{-1} \equiv M \cdot s^{-1}$

For k_2, $n = 1$, $k = \frac{1}{t} \cdot \frac{1}{(\text{conc})^{1-1}} = \frac{1}{t} = s^{-1}$

TOPIC 2
Order and Molecularity

18 For a first order reaction, the ratio of the time for 75% completion of a reaction to the time for 50% completion is .....
(Integer answer) **[2021, 31 Aug Shift-I]**

Ans. ***(2)***

For a first order reaction, rate constant is given as,

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

where, a = initial concentration of reactant and

$a - x$ = concentration of reactant after time t.

For 50% completion,

$$k = \frac{2.303}{t_{50\%}}\log\frac{100}{100-50} \quad ...(i)$$

For 75% completion,

$$k = \frac{2.303}{t_{75\%}}\log\frac{100}{100-75} \quad ...(ii)$$

From Eqs. (i) and (ii),

$$\frac{2.303}{t_{50\%}}\log\frac{100}{50} = \frac{2.303}{t_{75\%}}\log\frac{100}{25}$$

$$\frac{0.3010}{t_{50\%}} = \frac{0.6020}{t_{75\%}}$$

$$t_{75\%} = 2t_{50\%}$$

$$\therefore \quad \frac{t_{75\%}}{t_{50\%}} = \frac{2}{1}$$

19 The first order rate constant for the decomposition of $CaCO_3$ at 700 K is 6.36×10^{-3} s^{-1} and activation energy is 209 kJ mol^{-1}. Its rate constant (in s^{-1}) at 600 K is $x \times 10^{-6}$. The value of x is ..... .
(Nearest integer)
[Given, $R = 8.31$ JK^{-1}mol^{-1}, $\log 6.36 \times 10^{-3} = -2.19$, $10^{-4.79} = 1.62 \times 10^{-5}$]
[2021, 27 Aug Shift-II]

Ans. ***(16)***

According to Arrhenius theory,

$$k = Ae^{-E_a/RT}$$

(k is the rate constant, A is Arrhenius factor, E_a = Activation energy, T is absolute temperature and R is gas constant.)

$$\ln k = \ln A - \frac{E_a}{RT}$$

At temperature T_1,

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad ...(i)$$

At temperature T_2,

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad ...(ii)$$

Subtracting Eqs. (ii) from (i),

$$\ln k_1 - \ln k_2 = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$2.303\log\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\log\frac{k_1}{k_2} = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

At, $T_1 = 700$ K, $k_1 = 6.36 \times 10^{-3}$ s^{-1},

$E_a = 209$ kJ mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1}

At, $T_2 = 600$ K, $k_2 = x \times 10^{-6}$ s^{-1}

$$\log\frac{6.36 \times 10^{-3}}{x \times 10^{-6}} = \frac{209}{2.303 \times 8.314}\left(\frac{1}{600} - \frac{1}{700}\right)$$

$$= \frac{209}{2.303 \times 8.314}\left(\frac{100}{420000}\right)$$

$x = 16$.

20 For the first order reaction, $A \longrightarrow 2B$, 1 mole of reactant A gives 0.2 moles of B after 100 minutes. The half-life of the reaction is ..... min. (Round off to the nearest integer). [Use : ln 2 = 0.69, ln 10 = 2.3; properties of logarithms : $\ln x^y = y \ln x$; $\ln\left(\frac{x}{y}\right) = \ln x - \ln y$]

(Round off to the nearest integer)
[2021, 27 July Shift-II]

Ans. ***(656)***

	A	$\longrightarrow$	$2B$
Initial	1 mol		0
Final	$1-x$		$2x$
Given,	$2x = 0.2$	$\Rightarrow$	$x = 0.1$
$\therefore$Final	0.9		0.2

Now, according to first order kinetics

$$t = \frac{2.303}{k}\log_{10}\frac{[A_0]}{[A_t]} \quad ...(i)$$

$$t_{1/2} = \frac{0.691}{k} \quad ...(ii)$$

Eq. (i) divided by Eq. (ii).

$$\frac{t}{t_{1/2}} = \frac{2.303}{0.691}\log_{10}\frac{(1)}{(0.9)}$$

$$= \frac{1}{0.3}\log_{10}\left(\frac{10}{9}\right)$$

$$= \frac{1}{0.3}\left[\log_{10}10 - \log_{10}9\right]$$

$$= \frac{1}{0.3}\left[1 - \log_{10}9\right]$$

$$= \frac{1}{0.3}\left[1 - \log_{10}3^2\right]$$

$$= \frac{1}{0.3}\left[1 - 2\log_{10}3\right]$$

$$= \frac{1}{0.3}\left[1 - 2(0.477)\right]$$

$$= \frac{1}{0.3}\left[1 - 0.954\right]$$

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$$\frac{t}{t_{1/2}}=\frac{0.0457}{0.3}$$

$$t_{1/2}=\frac{3\times t}{0.457}=\frac{3\times 100}{0.457}\approx 656$$

21 For a reaction of order n, the unit of the rate constant is

[2021, 27 July Shift-I]

(a) $mol^{1-n}\,L^{1-n}\,s$ (b) $mol^{1-n}\,L^{2n}\,s^{-1}$
(c) $mol^{1-n}\,L^{n-1}\,s^{-1}$ (d) $mol^{1-n}\,L^{1-n}\,s^{-1}$

Ans. ***(c)***

The unit of rate constant (k) for a reaction of order n is

$$\text{Rate}=k\,[A]^n$$

or $$\text{Rate}=k\,[\text{Reactant}]^n$$

$$\Rightarrow \quad k=\frac{\text{Rate of reaction}}{[\text{Reactant}]^n}$$

$$=\frac{mol^1\,L^{-1}s^{-1}}{[mol^n/L^n]}$$

$$=mol^{1-n}L^{n-1}s^{-1}$$

Therefore, option (c) is correct.

22 The following data was obtained for chemical reaction given below at 975 K.

$$2NO(g)+2H_2(g)\rightarrow N_2(g)+2H_2O(g)$$

	[NO] mol L^{-1}	[H_2] mol L^{-1}	[Rate] mol L^{-1}
A.	8×10^{-5}	8×10^{-5}	7×10^{-9}
B.	24×10^{-5}	8×10^{-5}	2.1×10^{-8}
C.	24×10^{-5}	32×10^{-5}	8.4×10^{-8}

The order of the reaction with respect to NO is ..... . [Integer answer] **[2021, 26 Aug Shift-I]**

Ans. ***(1)***

Rate of the reaction $=K\,[NO]^x\,[H_2]^y$ where K is rate constant and x, y are order of reaction w.r.t. NO and H_2 respectively.

From observations A and B

$$7\times10^{-9}=K\,(8\times10^{-5})^x\,(8\times10^{-5})^y \quad ...(i)$$

and $$2.1\times10^{-8}=K\,(24\times10^{-5})^x\,(8\times10^{-5})^y \quad ...(ii)$$

Dividing Eqs. (i) by (ii)

$$\frac{7\times10^{-9}}{2.1\times10^{-8}}=\frac{K\,(8\times10^{-5})^x\,(8\times10^{-5})^y}{K(24\times10^{-5})^x\,(8\times10^{-5})^y}$$

$$\frac{1}{3}=\left(\frac{1}{3}\right)^x$$

$$x=1$$

$\therefore$ Order of reaction w.r.t. NO is 1.

23 For the reaction, $A+B\rightleftharpoons 2C$

The value of equilibrium constant is 100 at 298 K. If the initial concentration of all the three species is 1 M each, then the equilibrium concentration of C is $x\times10^{-1}$ M. The value of x is ..... . (Nearest integer)

[2021, 25 July Shift-I]

Ans. ***(25)***

According to given equilibrium reaction,

	A	+ B	$\rightleftharpoons$	$2C$
At $t=0$,	1	1		1
At $t=t$,	$1-x$	$1-x$		$1+2x$

So, equilibrium constant $(k)=\dfrac{[C]^2}{[A][B]}$

$$100=\frac{(1+2x)^2}{(1-x)(1-x)}$$

$$\frac{1+2x}{1-x}=10$$

$$1+2x=10-10x \Rightarrow x=\frac{3}{4}$$

Concentration of C at equilibrium, $[C]=1+2x$

Put value of x, we get

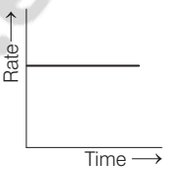
$$[C]=1+2\times\frac{3}{4}$$

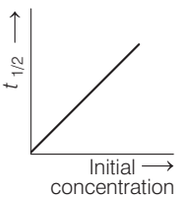
$$=1+\frac{3}{2}=2.5\text{ M}=25\times10^{-1}\text{ M}$$

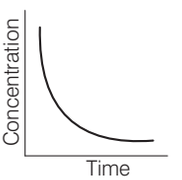
So, concentration of C is 25×10^{-1} M

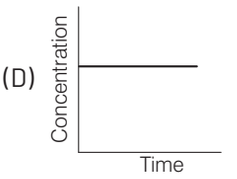
Hence, $x=25$.

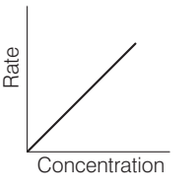
24 For the following graphs

(A) 

(B) 

(C) 

(D) 

(E) 

Choose from the options given below, the correct one regarding order of reaction is

[2021, 25 July Shift-I]

(a) (B) zero order (C) and (E) first order
(b) (A) and (B) zero order (E) first order
(c) (B) and (D) zero order (E) first order
(d) (A) and (B) zero order (C) and (E) first order

Ans. ***(b)***

For zero order reaction, $A_t=A_0-kt$

Here, A_t = concentration at time t

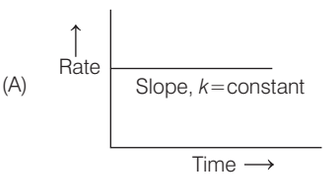
A_0 = initial concentration

k = rate constant

$$\text{Rate}=k[A]^0$$

$$\text{Rate}=k\text{ (constant)}$$

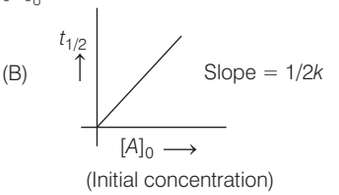
compare with, $y=mx+c$

(A) 

For zero order reaction,

$$t_{1/2}=\frac{[A]_0}{2k}$$

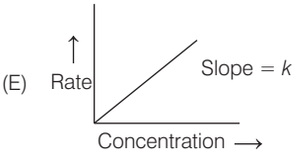
Slope for graph between $t_{1/2}$ and $[A]_0=1/2k$

(B) 

For first order reaction,

$$\text{Rate}=k[\text{concentration}]$$

$$\text{Slope}=k$$

(E) 

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25 $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

In the above first order reaction the initial concentration of N_2O_5 is 2.40×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 1 hour was 1.60×10^{-2} mol L^{-1}. The rate constant of the reaction at 318 K is ..... $\times 10^{-3}$ min^{-1}. (Nearest integer)
[Given : log3 = 0.477, log5 = 0.699]
[2021, 22 July Shift-II]

Ans. ***(7)***

For the reaction,

$$N_2O_5(g) \longrightarrow 2NO(g) + \frac{1}{2}O_2(g)$$

For a first order reaction, rate constant will be

$$k = \frac{2.303}{t}\log\frac{C_0}{C_t}$$

$$= \frac{2.303}{60}\log\frac{2.4 \times 10^{-2}}{1.6 \times 10^{-2}}$$

$$= 6.909 \times 10^{-3}$$

$$k = 7 \times 10^{-3}$$

$\therefore$ Hence, k value at 318 K is 7×10^{-3} min^{-1}.

26 A reaction has a half-life of 1 min. The time required for 99.9% completion of the reaction is ..... min (Round off to the nearest integer).
[Use : ln 2 = 0.69, ln 10 = 2.3]
[2021, 18 March Shift-II]

Ans. ***(10)***

Using formula,

$$k = \frac{1}{t}\ln\left(\frac{C_0}{C_t}\right)$$

As $k = \frac{\ln 2}{t_{1/2}}$

$t_{1/2} = 1$ min [Given]

$$\therefore \quad \frac{\ln 2}{1} = \frac{1}{t}\ln\left(\frac{100}{0.1}\right)$$

$$\Rightarrow \quad t = \frac{\ln 1000}{\ln 2}$$

$$t = \frac{3 \times 2.3}{0.69} = 10$$

27 For a certain first order reaction 32% of the reactant is left after 570 s. The rate constant of this reaction is ..... $\times 10^{-3}$ s^{-1}. (Round off to the nearest integer).
[Given, $\log_{10} 2 = 0.301$, ln 10 = 2.303]
[2021, 17 March Shift-I]

Ans. ***(2)***

For first order reaction,

$$k \times t = \ln\frac{A_0}{A_t} \qquad ...(i)$$

where, rate = rate constant

t = time

Initial conc. of reactant, $A_0 = 100$

Conc. of reactant after 't' time, $A_t = 32$

Put all values in equation (i)

$A_t = 32$

$$k \times 570 = \ln\frac{100}{32}$$

$$k \times 570 = 2.303\,(\log 10^2 - \log 2^5)$$

$$\Rightarrow \quad k = \frac{2.303}{570}(2 - 5\log 2)$$

$$= \frac{2.303}{570}[2 - (5 \times 0.3)]$$

$$= \frac{2.303}{570} \times 0.5$$

$$k = 2 \times 10^{-3}\ s^{-1}$$

28 *A* and *B* decompose *via* first order kinetics with half-lives 54.0 min and 18.0 min respectively. Starting from an equimolar non-reactive mixture of *A* and *B*, the time taken for the concentration of *A* to become 16 times that of *B* is ..... min.
(Round off to the nearest integer).
[2021, 16 March Shift-II]

Ans. ***(108)***

Given, $(t_{1/2})_1 = 54$ min

$(t_{1/2})_2 = 18$ min

A	*B*
$t = 0$, 'x' M	$t = 0$, 'x' M

To calculate, $[A_t] = 16 \times [B_t]$ ...(i)

time = ?

For Ist order reaction, $[A_t] = \frac{A_0}{(2)^n}$

n = number of half-lives

From Eq. (i),

$$[A_t] = 16 \times [B_t]$$

$$\frac{x}{(2)^{n_1}} = \frac{x}{(2)^{n_2}} \times 16$$

$$(2)^{n_2} = (2)^{n_1} \times (2)^4$$

$$\Rightarrow \quad n_2 = n_1 + 4$$

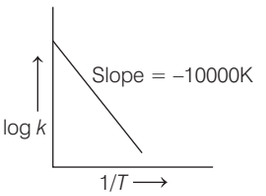
$$\frac{t}{(t_{1/2})_2} = \frac{t}{(t_{1/2})_1} + 4$$

$$\Rightarrow t\left(\frac{1}{18} - \frac{1}{54}\right) = 4$$

$$\Rightarrow \quad t = \frac{4 \times 18 \times 54}{36}$$

$$= 108 \text{ min}$$

29 For the reaction,
$aA + bB \rightarrow cC + dD$, the plot of $\log k$ *vs* $\frac{1}{T}$ is given below



The temperature at which the rate constant of the reaction is 10^{-4} s^{-1} is ..... K
(Rounded off to the nearest integer).
[Given : The rate constant of the reaction is 10^{-5} s^{-1} at 500 K]
[2021, 25 Feb Shift-I]

Ans. ***(526)***

According to Arrhenius equation,

$$\log K = \log A - \frac{E_a}{2.303\,RT}$$

Given, Slope $= \frac{E_a}{2.303\,R} = 10{,}000$

$$K_1 = 10^{-5}, K_2 = 10^{-4}$$

$$T_1 = 500 \text{ K}$$

$$\log_{10}\left[\frac{K_1}{K_2}\right] = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\left[\frac{10^{-4}}{10^{-5}}\right] = 10000\left[\frac{1}{500} - \frac{1}{T_2}\right]$$

$$\log 10 = 10000\left[\frac{1}{500} - \frac{1}{T_2}\right]$$

$$T_2 = 526.31 \simeq 526 \text{ K}$$

30 Sucrose hydrolyses in acid solution into glucose and fructose following first order rate law with a half-life of 3.33 h at 25°C. After 9 h, the fraction of sucrose remaining is f. The value of $\log_{10}\left(\frac{1}{f}\right)$ is ..... $\times 10^{-2}$
(Rounded off to the nearest integer).
[Assume, ln 10 = 2.303, ln 2 = 0.693] **[2021, 24 Feb Shift-II]**

Ans. ***(81)***

Given,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{1st order}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$t_{1/2} = \frac{10}{3}\text{ h}$$

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$t = 0, \quad a = [A]_0$ (initial conc.)

At $t = 9\,h \quad a - x = [A]_t$ [conc. at time t]

For using 1st order equation,

$$K = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$$

$$\Rightarrow \quad \frac{K \times t}{2.303} = \log\frac{[A]_0}{[A]_t}$$

$$\frac{\ln 2 \times 9}{10/3 \times 2.303} = \log\left(\frac{1}{F}\right)$$

$$\Rightarrow \quad \log\left(\frac{1}{F}\right) = 0.8124 \qquad \left(\because k = \frac{\ln 2}{t_{1/2}}\right)$$

$$\log\left(\frac{1}{F}\right) = 81.24 \times 10^{-2}$$

$$x = 81.24$$

or $x \approx 81$

31 Gaseous cyclobutene isomerises to butadiene in a first order process which has a 'k' value of 3.3×10^{-4} s^{-1} at 153°C. The time in minutes it takes for the isomerisation to proceed 40 % to completion at this temperature is ..... .

(Rounded off to the nearest integer) **[2021, 24 Feb Shift-I]**

Ans. ***(26)***

Cyclobutene $\longrightarrow H_2C{=}CH{-}CH{=}CH_2$ (1, 3-butadiene)

It is a first order isomerisation reaction. Integrated rate law for 1st order reaction is

$$kt = \ln\frac{[A]_0}{[A]_t} \qquad ...(i)$$

Here, k = rate constant

$[A]_0$ = initial concentration

$[A]_t$ = concentration at time 't'

Given, $k = 3.3 \times 10^{-4}\ s^{-1}$

$[A]_0 = 100$

$\Rightarrow \quad [A]_t = 100 - 40 = 60$

Put values in Eq. (i), we get

$$3.3 \times 10^{-4}\,s^{-1} \times t = \ln\frac{100}{60}$$

$$t = 1547.95\,s = 25.79\,min$$

$$(1\,min = 60\,s \text{ or } 1\,s = \frac{1}{60}\,min)$$

$= 26$ minutes

32 The results given in the below table were obtained during kinetic studies of the following reaction :

$$2A + B \rightarrow C + D$$

Experiment	$[A]$/mol L^{-1}	$[B]$/mol L^{-1}	Initial rate/mol L^{-1} min^{-1}
I	0.1	0.1	6.00×10^{-3}
II	0.1	0.2	2.40×10^{-2}
III	0.2	0.1	1.20×10^{-2}
IV	X	0.2	7.20×10^{-2}
V	0.3	Y	2.88×10^{-1}

X and Y in the given table are respectively **[2020, 2 Sep Shift-II]**

(a) 0.4, 0.4 (b) 0.4, 0.3

(c) 0.3, 0.4 (d) 0.3, 0.3

Ans. ***(c)***

Let, the rate law is : $r \propto [A]^a [B]^b$

$\therefore$ a and b are the order of reaction w.r.t A and B respectively.

$\Rightarrow$ Comparing first three (I, II, III) experiments :

$$\frac{r_{II}}{r_I} = \left(\frac{0.1}{0.1}\right)^a \times \left(\frac{0.2}{0.1}\right)^b$$

$$\Rightarrow \quad \frac{2.4 \times 10^{-2}}{6 \times 10^{-3}} = 1 \times 2^b$$

$$\Rightarrow \quad 2^b = 4 \Rightarrow b = 2$$

$$\frac{r_{III}}{r_I} = \left(\frac{0.2}{0.1}\right)^a \times \left(\frac{0.1}{0.1}\right)^2$$

$$\Rightarrow \quad \frac{1.2 \times 10^{-2}}{6 \times 10^{-3}} = 2^a \times 1$$

$$\Rightarrow \quad 2^a \times 2 \Rightarrow a = 1$$

$$\Rightarrow \quad r_I = k \times (0.1)^1 (0.1)^2$$

$$\Rightarrow \quad 6 \times 10^{-3} = k \times 10^{-3}$$

$$\Rightarrow \quad k = 6\,L^2\,mol^{-2}\,min^{-1}$$

$$\Rightarrow \quad \text{Expt. IV} : r_{II} = 6 \times (X)^1 \times (0.2)^2$$

$$\Rightarrow \quad 7.2 \times 10^{-2} = 6 \times (X) \times (4 \times 10^{-2})$$

$$\Rightarrow \quad X = 0.3\,mol\,L^{-1}$$

$$\Rightarrow \text{Ex pt. V} : r_V = 6 \times (0.3)^1 \times (Y)^2$$

$$\Rightarrow \quad 2.88 \times 10^{-1} = 6 \times 0.3 \times (Y)^2$$

$$\Rightarrow \quad Y = 0.4\,mol\,L^{-1}$$

33 Decomposition of X exhibits a rate constant of 0.05 µg/year. How many years are required for the decomposition of 5 µg of X into 2.5 µg? **[2019, 12 Jan Shift-I]**

(a) 20 (b) 25

(c) 40 (d) 50

Ans. ***(d)***

Given, rate constant (k) = 0.05 µg/year

Thus, from the unit of k, it is clear that the reaction is zero order. Now, we know that

half-life ($t_{1/2}$) for zero order reaction $= \frac{a_0}{2k}$

where, a_0 = initial concentration, k = rate constant

$$t_{1/2} = \frac{5\ \mu g}{2 \times 0.05\ mg/year}$$

$= 50$ years

Thus, 50 years are required for the decomposition of 5 µg of X into 2.5 µg.

34 It is true that **[2020, 3 Sep Shift-I]**

(a) a second order reaction is always a multistep reaction

(b) a zero order reaction is a multistep reaction

(c) a first order reaction is always a single step reaction

(d) a zero order reaction is a single step reaction

Ans. ***(b)***

Only statement (b) is true whereas all other statements are incorrect. A zero order reaction is a multistep reaction because in most of the zero order reactions, free radical is the intermediate which follow chain-initiation, chain-propagation and chain-termination like steps, e.g., free radical substitution reaction.

(a) A second order reaction is always a single step reaction, e.g., S_N2 and E_2 reactions.

(c) A first order reaction may be a multi-step reaction when intermediate of the reaction, like carbocation (I_1) gets rearranged into its most stable form (I_2).

Same is the case with (d).

So, options (a), (c) and (d) are not true.

35 If 75% of a first order reaction was completed in 90 minutes, 60% of the same reaction would be completed in approximately (in minutes) ..... .

(Take : $\log 2 = 0.30; \log 2.5 = 0.40$) **[2020, 4 Sep Shift-I]**

Ans. ***(60)***

Given, first order reaction,

$t_{75} = 90$ minute

$\Rightarrow \quad t_{60} = ?$

Consider the following reaction,

$$\underset{\text{(Reactant)}}{A} \longrightarrow \underset{\text{(Product)}}{B}$$

Time,	$t = 0$	100
$t_{15\%} = 90$ min		$(100 - 75) = 25$
$t_{60\%} = ?$		$(100 - 60) = 40$

For first order reaction,

$$t = \frac{2.303}{k}\log\left(\frac{a_0}{a}\right)$$

$[a_0$ = Initial concentration

a = Concentration$]$

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For 75%,

$$t_{75\%} = \frac{2.303}{k}\log\left(\frac{100}{25}\right) \quad ...(i)$$

$$\left[\begin{matrix}\text{Initial conc.} = 100\\ \text{Conc.} = 100 - 75 = 25\end{matrix}\right]$$

For 60%,

$$t_{60\%} = \frac{2.303}{k}\log\left(\frac{100}{40}\right) \quad ...(ii)$$

$$\left[\begin{matrix}\text{Initial conc.} = 100\\ \text{Conc.} = 100 - 60 = 40\end{matrix}\right]$$

On equating Eqs. (i) and (ii),

$$\frac{t_{60\%}}{t_{75\%}} = \frac{\frac{2.303}{k}\log\left(\frac{100}{40}\right)}{\frac{2.303}{k}\log\left(\frac{100}{25}\right)}$$

$$t_{60\%} = t_{75\%} \times \left(\frac{0.3979}{0.602}\right)$$

$$\Rightarrow \quad t_{60\%} = 90 \times \frac{0.3979}{0.602}$$

$$t_{60\%} = 59.48 \text{ minute}$$

$$\approx 60 \text{ min}$$

36 A flask contains a mixture of compounds *A* and *B*. Both compounds decompose by first-order kinetics. The half-life for *A* and *B* are 300 s and 180 s, respectively. If the concentrations of *A* and *B* are equal initially, the time required for the concentration of *A* to be four times that of *B* (in s) is (Use ln 2 = 0.693)

[2020, 5 Sep Shift-I]

(a) 120 (b) 180
(c) 300 (d) 900

Ans. ***(d)***

We know that, $N = N_0 e^{-Kt}$

K can be calculated as :

$$K = \frac{\ln 2}{t_{1/2}} \quad (\text{Here, } t_{1/2} = \text{half-life})$$

∵ The time required for the concentration of *A* to be four times that of *B*. Hence,

$$A = 4B$$

$$N_0 e^{\frac{-\ln 2\, t}{300}} = 4 \cdot N_0 e^{\frac{-\ln 2\, t}{180}}$$

$$\Rightarrow \quad -\frac{\ln 2 t}{300} = \ln 4 - \frac{\ln 2 t}{180}$$

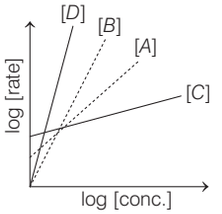
$$\Rightarrow \quad \ln 2 t\left[\frac{1}{180} - \frac{1}{300}\right] = 2\ln 2;$$

$$t = \frac{2 \times 180 \times 300}{120} = 900 \text{ s}$$

37 Consider the following reactions

$A \rightarrow$ P1; $B \rightarrow$ P2; $C \rightarrow$ P3; $D \rightarrow$ P4,

The order of the above reactions are *a*, *b*, *c* and *d*, respectively. The following graph is obtained when log[rate] vs log[conc.] are plotted :



Among the following, the correct sequence for the order of the reactions is **[2020, 6 Sep Shift-I]**

(a) $D > A > B > C$ (b) $A > B > C > D$
(c) $C > A > B > D$ (d) $D > B > A > C$

Ans. ***(d)***

We know that,

Rate = k(concentration)^n

[n = order of reaction and k = rate constant]

Taking log both side,

log (Rate) = log k + $n$log [concentration]

Slope of graph is the order of reaction greater the slope, greater is the order of reaction.

∴Correct sequence for the order of reaction is $D > B > A > C$.

Hence, the correct option is (d).

38 During the nuclear explosion, one of the products is ^{90}Sr with half-life of 6.93 years. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby in place of Ca, how much time, in years, is required to reduce it by 90% if it is not lost metabolically ..... .

[2020, 7 Jan Shift-I]

Ans. ***(23.03)***

Radioactive decay follows first order kinetics.

∴ Time taken for decay from N_0 to N_t is (N = number of nuclei)

$$t = \frac{1}{\lambda}\ln\frac{N_0}{N_t}$$

$$t = \frac{1}{\lambda} \times 2.303 \log\frac{N_0}{N_t} \quad ...(i)$$

Also, we know λ = (decay constant)

$$= \frac{0.693}{t_{1/2}}$$

where, $t_{1/2} = 6.93$ yr (given)

Also, we know 90% nuclei are decayed

$$\therefore \quad \frac{N_0}{N_t} = \frac{100}{10} = 10$$

Put the values of λ and $\frac{N_0}{N_t}$ in Eq. (i), we get

$$\therefore t = \frac{6.93}{0.693} \times 2.303 \times \log 10 = 23.03 (\text{yr})$$

39 For the reaction, $2A + B \rightarrow C$, the values of initial rate at different reactant concentrations are given in the table below.

The rate law for the reaction is

[2019, 8 April Shift-I]

[*A*] (mol L^{-1})	[*B*] (mol L^{-1})	Initial rate (mol L^{-1}s^{-1})
0.05	0.05	0.045
0.10	0.05	0.090
0.20	0.10	0.72

(a) rate = k [A] [B]^2 (b) rate = k [A]^2[B]^2
(c) rate = k [A] [B] (d) rate = k [A]^2[B]

Ans. ***(a)***

Let the rate equation be $k[A]^x [B]^y$

From Ist values,

$$0.045 = k[0.05]^x [0.05]^y \quad ...(i)$$

From 2nd values,

$$0.090 = k[0.10]^x [0.05]^y \quad ...(ii)$$

From 3rd values,

$$0.72 = k[0.20]^x [0.10]^y \quad ...(iii)$$

On dividing equations (i) by (ii), we get

$$\frac{0.045}{0.09} = \left[\frac{0.05}{0.10}\right]^x$$

$$\Rightarrow \quad \left[\frac{0.05}{0.10}\right]^1 = \left[\frac{0.05}{0.10}\right]^x$$

$$\therefore \quad x = 1$$

Similarly on dividing Eq. (ii) by (iii) we get

$$\frac{0.09}{0.72} = \left[\frac{0.1}{0.2}\right]^x \left[\frac{0.05}{0.10}\right]^y$$

$$\Rightarrow \quad \frac{0.01}{0.08} = \frac{0.1}{0.2}\left[\frac{0.05}{0.1}\right]^y$$

$$0.25 = \left[\frac{0.05}{0.10}\right]^y$$

$$\Rightarrow \quad 0.25 = [0.5]^y$$

$$[0.5]^2 = [0.5]^y$$

$$\Rightarrow \quad y = 2$$

Hence, the rate law for the reaction

$$\text{Rate} = k[A][B]^2$$

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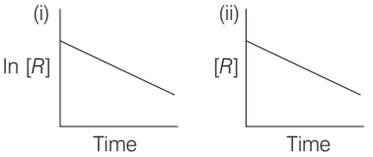
40 The given plots represent the variation of the concentration of a reaction *R* with time for two different reactions (i) and (ii). The respective orders of the reactions are **[2019, 9 April Shift-I]**



(a) 1, 1 (b) 0, 2
(c) 0, 1 (d) 1, 0

Ans. ***(d)***

In first order reaction, the rate expression depends on the concentration of one species only having power equal to unity.

$$nr \longrightarrow \text{products}$$

$$\frac{-d[r]}{dt} = k[r]$$

On integration, $-\ln[r] = kt - \ln[r_0]$

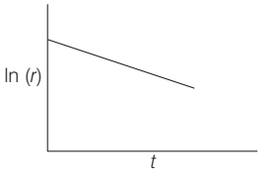
or $\ln(r) = \ln(r_0) - kt$

$\Rightarrow \quad y = c + mx$

m = slope $= -k$ (negative);

c = intercept $= \ln(r_0)$

The graph for first order reactions is



In zero order reaction,

$$[r] \longrightarrow \text{product}$$

$$\therefore \quad \frac{-d[r]_t}{dt} = k \text{ or } -d[r]_t = kdt$$

On integrating, $-[r]_t = kt + c$

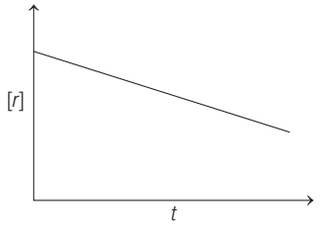
If $t = 0, [r]_t = [r]_0$

$\therefore \quad -[r]_t = kt - [r]_0$

$\Rightarrow \quad [r]_t = [r]_0 - kt$

Thus, the graph plotted between $[r]_t$ and t gives a straight line with negative slope $(-k)$ and intercept equal to $[r]_0$.

The graph for zero order reaction is



41 The following results were obtained during kinetic studies of the reaction;

$$2A + B \longrightarrow \text{Products}$$

Experiment	[A] (mol L^{-1})	[B] (mol L^{-1})	Initial rate of reaction (in mol L^{-1} min^{-1})
I.	0.10	0.20	6.93×10^{-3}
II.	0.10	0.25	6.93×10^{-3}
III.	0.20	0.30	1.386×10^{-2}

The time (in minutes) required to consume half of *A* is **[2019, 9 Jan Shift-I]**

(a) 5 (b) 10
(c) 100 (d) 1

Ans. ***(b)***

Let, the rate expression is $r \propto [A]^a [B]^b$.

From experiment I,

$$\frac{r_2}{r_1} = \left(\frac{0.1}{0.1}\right)^a \times \left(\frac{0.25}{0.20}\right)^b$$

$$\Rightarrow \quad \frac{6.93 \times 10^{-3}}{6.93 \times 10^{-3}} = 1 \times \left(\frac{5}{4}\right)^b$$

$$\Rightarrow \quad 1 = \left(\frac{5}{4}\right)^b \Rightarrow \left(\frac{5}{4}\right)^0 = \left(\frac{5}{4}\right)^b \Rightarrow b = 0$$

From experiment II,

$$\frac{r_3}{r_1} = \left(\frac{0.2}{0.1}\right)^a \times \left(\frac{0.30}{0.20}\right)^b$$

$$\Rightarrow \quad \frac{1.386 \times 10^{-2}}{0.693 \times 10^{-2}} = (2)^a \times (1.5)^0$$

$$\Rightarrow \quad 2 = 2^a \times 1 \Rightarrow 2^1 = 2^a \Rightarrow a = 1$$

$\Rightarrow$ So, $r \propto [A]^1 [B]^0 \Rightarrow r \propto [A]$

Order of the reaction $(n) = 1$

$\Rightarrow$ Now, let for the 1st experiment,

$$r_1 = k \cdot [A]$$

$$\Rightarrow \quad k = \frac{r_1}{[A]} = \frac{6.93 \times 10^{-3}}{0.1}$$

$$= 6.93 \times 10^{-2} \text{ s}^{-1}$$

$$\Rightarrow \quad t_{50} = \frac{0.693}{k}$$

$$= \frac{0.693}{6.93 \times 10^{-2}} = 10 \text{ s}$$

42 For the following reaction,

$2A + B \longrightarrow$ products

When concentration of both (*A* and *B*) becomes double, then rate of reaction increases from 0.3 mol L^{-1} s^{-1} to 2.4 mol L^{-1} s^{-1}.

When concentration of only *A* is doubled, the rate of reaction increases from 0.3 mol L^{-1} s^{-1} to 0.6 mol L^{-1} s^{-1}.

Which of the following is true?

(a) The whole reaction is of 4th order
(b) The order of reaction w.r.t. *B* is one
(c) The order of reaction w.r.t. *B* is 2
(d) The order of reaction w.r.t. *A* is 2 **[2019, 9 Jan Shift-II]**

Ans. ***(c)***

For the reaction, $2A + B \longrightarrow$ products.

Let, the rate expression is $r \propto [A]^a [B]^b$

Expt 1 $\quad \frac{r_2}{r_1} = \left(\frac{2A}{A}\right)^a \left(\frac{2B}{B}\right)^b$

$$\Rightarrow \quad \frac{2.4}{0.3} = 2^a \times 2^b \Rightarrow 2^3 = 2^{a+b}$$

$$\Rightarrow \quad 3 = a + b \qquad \ldots (i)$$

Expt 2 $\quad \frac{r_2}{r_1} = \left(\frac{2A}{A}\right)^a \left(\frac{B}{B}\right)^b$

$$\Rightarrow \quad \frac{0.6}{0.3} = 2^a \times 1$$

$$\Rightarrow \quad 2^1 = 2^a \Rightarrow a = 1 \qquad \ldots (ii)$$

$\therefore$ From Eq. (i), $1 + b = 3 \Rightarrow b = 2$

$\Rightarrow$ Order of the reaction $(n) = a + b = 1 + 2 = 3$

$\Rightarrow$ Order of the reaction wrt. $A = 1$

$\Rightarrow$ Order of the reaction wrt. $B = 2$

43 The reaction, $2X \rightarrow B$ is a zeroth order reaction. If the initial concentration of *X* is 0.2 M, the half-life is 6 h. When the initial concentration of *X* is 0.5 M, the time required to reach its final concentration of 0.2 M will be **[2019, 11 Jan Shift-II]**

(a) 7.2 h (b) 18.0 h
(c) 12.0 h (d) 9.0 h

Ans. ***(b)***

For zero order reaction,

$$[A_0] - [A_t] = kt \qquad \ldots (i)$$

where,

$[A_0]$ = initial concentration

$[A_t]$ = final concentration at time '*t*'

k = rate constant

Also, for zero order reaction, $t_{1/2} = \frac{[A_0]}{2k}$

Given, $t_{1/2} = 6$ h and $[A_0] = 0.2$ M

$\therefore \quad 6 = \frac{0.2}{2k}$ or $k = \frac{0.2}{2 \times 6} = \frac{1}{60}$

Now, from Eq. (i)

$$[A_0] - [A_t] = kt$$

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Given, $[A_0] = 0.5\,M, [A_t] = 0.2\,M$

$\therefore \quad 0.5 - 0.2 = \frac{1}{60} \times t \qquad \left[\because k = \frac{1}{60}\right]$

$0.3 = \frac{1}{60} \times t$

$\Rightarrow \quad t = 0.3 \times 60 = 18\,h$

44 At 518°C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s^{-1} when 5% had reacted and 0.5 Torr s^{-1} when 33% had reacted. The order of the reaction is : **[JEE Main 2018]**

(a) 2 (b) 3
(c) 1 (d) 0

Ans. ***(a)***

For the reaction,

$$CH_3CHO(g) \xrightarrow{\text{Decomposes}} CH_4 + CO$$

Let order of reaction with respect to CH_3CHO is m.

Its given, $r_1 = 1$ torr/sec. when CH_3CHO is 5% reacted i.e. 95% unreacted.

Similarly, $r_2 = 0.5$ torr/sec when CH_3CHO is 33% reacted i.e., 67% unreacted.

Use the formula,

$$r \propto (a - x)^m$$

where $(a - x)$ = amount unreacted

so, $\frac{r_1}{r_2} = \frac{(a - x_1)^m}{(a - x_2)^m}$ or $\frac{r_1}{r_2} = \left[\frac{a - x_1}{a - x_2}\right]^m$

Now putting the given values

$$\frac{1}{0.5} = \left(\frac{0.95}{0.67}\right)^m$$

$\Rightarrow \quad 2 = (1.41)^m$ or $m = 2$

45 Decomposition of H_2O_2 follows a first order reaction. In 50 min, the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be **[JEE Main 2016]**

(a) 6.93×10^{-4} mol min^{-1}
(b) 2.66 L min^{-1} at STP
(c) 1.34×10^{-2} mol min^{-1}
(d) 6.93×10^{-2} mol min^{-1}

Ans. ***(a)***

For first order reaction,

$k = \frac{2.303}{t} \log \frac{a}{a - x}$

Given, $t = 50$ min, $a = 0.5$ M,
$a - x = 0.125$ M

$\therefore \quad k = \frac{2.303}{50} \log \frac{0.5}{0.125} = 0.0277\,min^{-1}$

Now, as per reaction

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$-\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$$

Rate of reaction, $-\frac{d[H_2O_2]}{dt} = k[H_2O_2]$

$\therefore \quad \frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}k[H_2O_2] \qquad ...(i)$

When the concentration of $[H_2O_2]$ reaches 0.05 M,

$\frac{d[O_2]}{dt} = \frac{1}{2} \times 0.0277 \times 0.05$ [from Eq. (i)]

or $\frac{d[O_2]}{dt} = 6.93 \times 10^{-4}$ mol min^{-1}

Alternative Method

In fifty minutes, the concentration of H_2O_2 decreases from 0.5 to 0.125 M or in one half-life, concentration of H_2O_2 decreases from 0.5 to 0.25 M. In two half-lives, concentration of H_2O_2 decreases from 0.5 to 0.125 M or $2t_{1/2} = 50$ min

$t_{1/2} = 25$ min $\Rightarrow k = \left(\frac{0.693}{25}\right) min^{-1}$

or $\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{k[H_2O_2]}{2}$

$= 6.93 \times 10^{-4}$ mol min^{-1}

46 For the non-stoichiometric reaction, $2A + B \longrightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K. **[JEE Main 2014]**

Initial concentration (A)	Initial concentration (B)	Initial rate of formation of C (mol L^{-1} s^{-1})
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

(a) $\frac{dc}{dt} = k[A][B]$ (b) $\frac{dc}{dt} = k[A]^2[B]$

(c) $\frac{dc}{dt} = k[A][B]^2$ (d) $\frac{dc}{dt} = k[A]$

Ans. ***(d)***

Rate law equation is given by,

$$\frac{dc}{dt} = k[A]^x[B]^y$$

$\therefore \frac{dc}{dt}$ for C at various concentrations are

$1.2 \times 10^{-3} = k(0.1)^x(0.1)^y$ ...(i)

$1.2 \times 10^{-3} = k(0.1)^x(0.2)^y$ ...(ii)

$2.4 \times 10^{-3} = k(0.2)^x(0.1)^y$ ...(iii)

Solving for x [divide Eq. (iii) by Eq. (i)]

$$\frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k(0.2)^x(0.1)^y}{k(0.1)^x(0.1)^y}$$

$2 = (2)^x \Rightarrow x = 1$

Solving for y [divide Eq. (iii) by Eq. (i)]

$$\frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k(0.2)^x(0.1)^y}{k(0.1)^x(0.2)^y}$$

$\Rightarrow \quad 2 = (2)^x\left(\frac{0.1}{0.2}\right)^y$

Put $x = 1$ in above Eq., we get

$$2 = (2)^1\left(\frac{0.1}{0.2}\right)^y \Rightarrow 1 = (0.5)^y$$

$(1)^0 = (0.5)^y \Rightarrow y = 0$

Thus, $\frac{dc}{dt} = k[A]^1[B]^0 \Rightarrow \frac{dc}{dt} = k[A]^1$

47 For a first order reaction, $(A) \longrightarrow$ products the concentration of A changes from 0.1 M to 0.025 M in 40 min. The rate of reaction when the concentration of A is 0.01 M is **[AIEEE 2012]**

(a) 1.73×10^{-5} M / min
(b) 3.47×10^{-4} M / min
(c) 3.47×10^{-5} M / min
(d) 1.73×10^{-4} M / min

Ans. ***(b)***

Rate constant for the first order reaction is given by

$$k = \frac{2.303}{t} \log\left(\frac{a}{a - x}\right)$$

$a = 0.1$ M

$(a - x) = 0.025$ M $\Rightarrow t = 40$ min

$\therefore \quad k = \frac{2.303}{40} \log \frac{0.1}{0.025\,M}$

$= 0.0347\,min^{-1}$

$\text{Rate} = \left(\frac{dx}{dt}\right) = k[A]^1$

$= 0.0347 \times 0.1$

$= 3.47 \times 10^{-4}$ M min^{-1}

48 The time for half-life period of a certain reaction, $A \longrightarrow$ products is 1 h. When the initial concentration of the reactant 'A' is 2.0 mol L^{-1}, how much time does it take for its

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concentration to come from 0.50 to 0.25 mol L^{-1}, if it is a zero order reaction? **[AIEEE 2010]**

(a) 4 h (b) 0.5 h (c) 0.25 h (d) 1 h

Ans. ***(c)***

Half- life for a zero order reaction is given by

$$t_{1/2} = \frac{[A_0]}{2k} \quad [\text{where } [A_0] = \text{initial concentration of reactant}]$$

$$\Rightarrow \quad k_0 = \frac{[A]_0}{2t_{1/2}} = \frac{2.0 \text{ mol L}^{-1}}{2 \times 1 \text{h}}$$

$$= 1.0 \text{ mol L}^{-1} \text{ h}^{-1}$$

Rate constant for a zero order reaction is given by

$$k = \frac{1}{t}[(A_0) - (A)] \Rightarrow t = \frac{1}{k}[(A_0) - (A)]$$

$$t = \frac{(0.50) - (0.25) \text{ mol L}^{-1}}{1 \text{ mol L}^{-1} \text{ h}^{-1}}$$

$$\Rightarrow \quad t = 0.25 \text{ h}$$

49 The half-life period of a first order chemical reaction is 6.93 min. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301) **[AIEEE 2009]**

(a) 230.3 min (b) 23.03 min
(c) 46.06 min (d) 460.6 min

Ans. ***(c)***

$$\text{Half-life} = 6.93 \text{ min}, k_1 = \frac{0.693}{6.93} = 0.1 \text{ min}^{-1}$$

Rate constant for the first order reaction is given by

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

where, $[A_0]$ = initial concentration

$[A]$ = final concentration

$$0.1 = \frac{2.303}{t} \times \log \frac{100}{1}$$

$$0.1 = \frac{2.303}{t} \log 10^2$$

$$t = \frac{2.303 \times 2}{0.1} \times 2 \log 10 = 46.06 \text{ min}$$

50 Consider the reaction, $2A + B \rightarrow$ product. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is **[AIEEE 2007]**

(a) L mol^{-1} s^{-1} (b) no unit
(c) mol L^{-1} s^{-1} (d) s^{-1}

Ans. ***(a)***

$$2A + B \longrightarrow \text{Products}$$

$[B]$ is doubled, half-life didn't change.

Half-life is independent of change in concentration of reactant *i.e.,* first order

First order *wrt* to B

When $[A]$ is doubled, rate increased by two times.

$\Rightarrow$ First order *wrt* A

Hence, net order of reaction = 1 + 1 = 2

Unit for the rate constant = $\text{conc}^{(1-n)}\, t^{-1}$

$$= (\text{mol L}^{-1})^{-1} \cdot \text{s}^{-1} = \text{L mol}^{-1} \text{ s}^{-1}$$

51 A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is ten times the permissible value, after how many days will it be safe to enter the room? **[AIEEE 2007]**

(a) 1000 days (b) 300 days
(c) 10 days (d) 100 days

Ans. ***(d)***

$$\text{Activity} \propto N \Rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$

or $$\frac{1}{10} = \left(\frac{1}{2}\right)^n \text{ or } 10 = 2^n$$

Taking log on both sides

$$\log 10 = n \log 2 \Rightarrow n = \frac{1}{0.301} = 3.32$$

$$\text{Time} = n \times \text{half-life}$$

$$= 3.32 \times 30$$

$$= 99.6 \text{ days} \approx 100 \text{ days}$$

Alternate method

Let the activity of safe working is A.

Given, $A_0 = 10\,[A]$

Radioactivity decay is the first order reaction.

Let the activity of safe working is A.

It is given that, $A_0 = 10\,[A]$

Half-life of a first order reaction is given by

$$t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

Rate constant for a first order reaction is given by,

$$k = \frac{2.303}{t} \log \frac{A_0}{A}$$

$$t = \frac{2.303}{k} \log \frac{A_0}{A} = \frac{2.303}{(0.693/30)} \log \frac{10\,[A]}{[A]}$$

$$= \frac{2.303}{(0.693/30)} \log 10$$

$$= 99.69 \text{ days}$$

$$\approx 100 \text{ days}$$

52 A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will

(a) remain unchanged **[AIEEE 2006]**
(b) triple
(c) increase by a factor of 4
(d) double

Ans. ***(c)***

$$r \propto [\text{CO}]^2;\ r' \propto [2\text{CO}]^2;\ \ r' \propto 4[\text{CO}]^2$$

Hence, $$\frac{r'}{r} = \frac{4[\text{CO}]^2}{[\text{CO}]^2} \text{ or } r' = 4r$$

53 The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr

$$\text{NO}(g) + \text{Br}_2(g) \rightleftharpoons \text{NOBr}_2(g)$$

$$\text{NOBr}_2(g) + \text{NO}(g) \longrightarrow 2\text{NOBr}(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO (g) is **[AIEEE 2006]**

(a) 1 (b) 0
(c) 3 (d) 2

Ans. ***(d)***

$$\text{Rate} = k[\text{NOBr}_2][\text{NO}] \quad \ldots(\text{i})$$

But $NOBr_2$ is in equilibrium.

$$\therefore \quad K_{eq} = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$$

$$[\text{NOBr}_2] = K_{eq}[\text{NO}][\text{Br}_2]$$

Putting the $[NOBr_2]$ in Eq. (i), we get

$$\text{Rate} = k \cdot K_{eq}[\text{NO}][\text{Br}_2][\text{NO}]$$

Hence, $$\text{Rate} = k \cdot K_{eq}[\text{NO}]^2[\text{Br}_2]$$

$$\text{Rate} = k'[\text{NO}]^2[\text{Br}_2]$$

where $$k' = k \cdot K_{eq}$$

54 A reaction involving two different reactants can never be **[AIEEE 2005]**

(a) bimolecular reaction
(b) second order reaction
(c) first order reaction
(d) unimolecular reaction

Ans. ***(d)***

There are two different reactants (say A and B).

$$A + B \longrightarrow \text{product}$$

Thus, it is a bimolecular reaction.

If $$\frac{dx}{dt} = k[A][B]$$

It is second order reaction.

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If $\left(\frac{dx}{dt}\right) = k[A] = k[B]$

It is first order reaction.

Molecularity is independent of rate but is the sum of the reacting substances.

Thus, it cannot be unimolecular reaction.

55 $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to 3/4 of its initial value. If the rate constant for a first order reaction is k, the $t_{1/4}$ can be written as **[AIEEE 2005]**

(a) 0.75 / k (b) 0.69 / k
(c) 0.29 / k (d) 0.10 / k

Ans. ***(c)***

	$A \longrightarrow$	Product
Initially	a	0
After time t	$(a-x)$	x
After $t_{1/4}$	$\left(a-\frac{a}{4}\right)$	$\frac{a}{4}$

For first order kinetics,

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

$$\Rightarrow \quad k = \frac{2.303}{t_{1/4}}\log\frac{a}{\frac{3a}{4}}$$

$$t_{1/4} = \frac{2.303\log\frac{4}{3}}{k} = \frac{0.29}{k}$$

56 In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is **[AIEEE 2004]**

(a) 30 min (b) 15 min
(c) 7.5 min (d) 60 min

Ans. ***(a)***

Order = 1

Concentration changes from 0.8 M to 0.4 M in (50%).

15 min, thus half-life = 15 min = T_{50}

A change from 0.1 M to 0.025 is 75% and for first order reaction

$$T_{75} = 2 \times T_{50} = 2 \times 15 = 30 \text{ min}$$

Alternate method

$$T_{50} = 15 \text{ min} \Rightarrow k = \frac{2.303\log 2}{T_{50}}$$

$$= \frac{2.303\log 2}{15}$$

$$a = 0.1 \text{ M} \Rightarrow (a-x) = 0.025 \text{ M}$$

$$\text{For first order, } k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

$$\frac{2.303\log 2}{15} = \frac{2.303}{t}\log\frac{0.1}{0.025}$$

$$= \frac{2.303}{t}\log 4$$

$$\therefore \frac{2.303\log 2}{15} = \frac{2\times 2.303\log 2}{t}$$

$$\Rightarrow \quad t = 30 \text{ min}$$

57 The rate law for a reaction between the substances A and B is given by rate $= k[A]^n[B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as **[AIEEE 2003]**

(a) $\frac{1}{2^{m+n}}$ (b) $(m+n)$
(c) $(n-m)$ (d) $2^{(n-m)}$

Ans. ***(d)***

$$\text{Rate, } r = k[A]^n[B]^m$$

On doubling $[A]$ and halving $[B]$, the rate becomes

$$r' = k[2A]^n[1/2\,B]^m$$

$$\Rightarrow \frac{r'}{r} = \frac{k[2A]^n[1/2\,B]^m}{k[A]^n[B]^m}$$

$$= \frac{(2)^n}{(2)^m} = (2)^n\cdot(2)^{-m} = (2)^{n-m}$$

58 For the reaction system,

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO; the rate of reaction will **[AIEEE 2003]**

(a) diminish to one-fourth of its initial value
(b) diminish to one-eighth of its initial value
(c) increase to eight times of its initial value
(d) increase to four times of its initial value

Ans. ***(c)***

$$\left(\frac{dx}{dt}\right) = k[NO]^2[O_2]$$

$$= k\left(\frac{n_{NO}}{V}\right)^2\left(\frac{n_{O_2}}{V}\right)$$

$$\left(\frac{dx}{dt}\right) = \frac{k}{V^3}(n_{NO})^2(n_{O_2})$$

$$= \frac{k(n_{NO})^2(n_{O_2})}{(V/2)^3} = 8\left(\frac{dx}{dt}\right)$$

59 Rate constant, k of the first order reaction when initial concentration (C_0) and concentration (C_t) at time t, is given by equation

$kt = \log C_0 - \log C_t$

Graph is a straight line if we plot **[AIEEE 2002]**

(a) t vs $\log C_0$ (b) t vs $\log C_t$
(c) t^{-1} vs $\log C_t$ (d) $\log C_0$ vs $\log C_t$

Ans. ***(b)***

$$kt = -\log_e C_t + \log_e C_0$$

$$t = -\frac{1}{k}\log_e C_t + \log_e C_0$$

$y = mx + c$, straight line, negative slope.

60 H_2 gas is adsorbed on the metal surface like tungsten. This follows ..... order reaction. **[AIEEE 2002]**

(a) third (b) second
(c) zero (d) first

Ans. ***(c)***

Most of the reaction which takes place on the surface of heterogeneous catalyst proceeds being independent of concentration.

61 For a reaction $A + 2B \longrightarrow C$, rate is given by $+\frac{d[C]}{dt} = k[A][B]$, hence the order of the reaction is **[AIEEE 2002]**

(a) 3 (b) 2
(c) 1 (d) 0

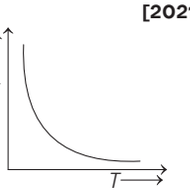
Ans. ***(b)***

Rate of the reaction depend upon the concentration of A and B both, hence it is a second order reaction.

TOPIC 3

Arrhenius Theory, Activation Energy and Collision Theory of Bimolecular Gaseous Reaction

62 Which one of the following given graphs represents the variation of rate constant (k) with temperature (T) for an endothermic reaction? **[2021, 1 Sep Shift-II]**

(a) 

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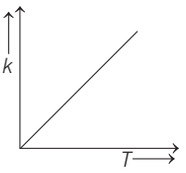
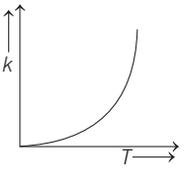
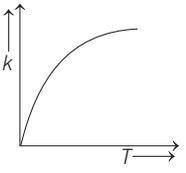
(b) 

(c) 

(d) 

Ans. ***(c)***

According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

As the temperature increases, rate constant k also increases which will generally speed up the process (increase the rate). So, graph will exponentially increases as in option (c).

63 For the reaction $A \rightarrow B$, the rate constant k (in s^{-1}) is given by

$$\log_{10} k = 20.35 - \frac{(2.47 \times 10^3)}{T}.$$

The energy of activation in kJ mol^{-1} is ..... (Nearest integer)

[Given : $R = 8.314\ J\ K^{-1}\ mol^{-1}$]

[2021, 31 Aug Shift-II]

Ans. ***(47)***

According to Arrhenius theory,

$$\log k = \log A \frac{-E_a}{2.303RT} \quad ...(i)$$

$$\log_{10} k = 20.35 - \frac{2.47 \times 10^3}{T} \quad ...(ii)$$

$$\frac{-2.47 \times 10^3}{T} = -\frac{E_a}{2.303RT}$$

Comparing Eqs. (i) and (ii),

$$E_a = 2.47 \times 2.303 \times 8.314$$
$$= 47.29\ kJ/mol \simeq 47\ kJ/mol$$

64 The inactivation rate of a viral preparation is proportional to the amount of virus. In the first minute after preparation, 10% of the virus is inactivated. The rate constant for viral inactivation is ..... × $10^{-3}\ min^{-1}$. (Nearest integer)

[Use: $\ln 10 = 2.303$; $\log_{10} 3 = 0.477$; property of logarithm : $\log x^y = y \log x$] **[2021, 20 July Shift-I]**

Ans. ***(106)***

Unit of rate constant is min^{-1}, so it must be a first order reaction.

For first order reaction,

$$k \times t = 2.303 \log \frac{A_0}{A_t}$$

k is the rate constant t is the time

A_0 is the initial conc.

A_t is the conc. at time, t

Using formula,

$$A_0 = 100, \quad A_t = 90 \text{ in } 1 \text{ min}$$

$$\text{So, } K \times 1 = 2.303 \times \log \frac{100}{90}$$
$$= 2.303 \times (\log 10 - 2 \log 3)$$
$$= 2.303 \times (1 - 2 \times 0.477)$$
$$= 0.10593 = 105.93 \times 10^{-3}$$
$$\approx 106$$

Hence, the rate constant for viral inactivation is 106.

65 The decomposition of formic acid on gold surface follows first order kinetics. If the rate constant at 300K is $1.0 \times 10^{-3}\ s^{-1}$ and the activation energy, $E_a = 11.488\ kJ\ mol^{-1}$, the rate constant at 200 K is ..... $\times 10^{-5}\ s^{-1}$ (Round off to the nearest integer).

[Given, $R = 8.314\ J\ mol^{-1}\ K^{-1}$]

[2021, 16 March Shift-I]

Ans. ***(10)***

Given, $T_1 = 200\ K, T_2 = 300\ K$

E_a = Activation energy = 11.488 kJ/mol

Rate constant (k_2) at 300 K = $10^{-3}\ s^{-1}$

To find = rate constant (k_1) at 200 K

We know,

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log \frac{10^{-3}}{k_1} = \frac{11.488 \times 10^3}{2.303 \times 8.314}\left(\frac{1}{200} - \frac{1}{300}\right)$$

$$\log \frac{10^{-3}}{k_1} = 1$$

$$\log \frac{10^{-3}}{k_1} = \log 10$$

$$\Rightarrow \quad k_1 = 10^{-4}$$
$$= 10 \times 10^{-5}\ s^{-1}$$

66 If the activation energy of a reaction is 80.9 kJ mol^{-1}, the fraction of molecules at 700 K, having enough energy to react to form products is e^{-x}. The value of x is .....

(Rounded off to the nearest integer)

[Use, $R = 8.31\ JK^{-1}\ mol^{-1}$].

[2021, 26 Feb Shift-II]

Ans. ***(14)***

According to Arrhenius equation, the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a (activation energy).

$$\Rightarrow \quad e^{E_a/RT} = e^{\frac{-80.9 \times 1000}{8.31 \times 700}} = e^{-13.90}$$
$$\simeq e^{-14} = e^{-x}$$
$$x = 14$$

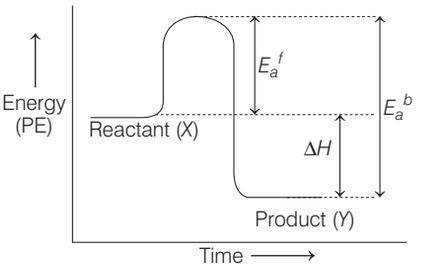
$[\because E_a = 80.9 kJ\ mol^{-1}$
$= 80.9 \times 1000 J\ mol^{-1}, \ R = 8.31 J\ mol^{-1}\ K^{-1}]$

67 An exothermic reaction $X \rightarrow Y$ has an activation energy 30 kJ mol^{-1}. If energy change ΔE during the reaction is –20 kJ mol^{-1}, then the activation energy for the reverse reaction in kJ is ..... .

[2021, 26 Feb Shift-I]

Ans. ***(50)***

$X \longrightarrow Y$, it is an exothermic reaction whose ΔE or $\Delta H = -20\ kJ\ mol^{-1}$



Given, activation energy of the forward reaction ($X \rightarrow Y$),

$$E_a^f = 30\ kJ\ mol^{-1}$$

Activation energy of the backward or reverse reaction ($Y \rightarrow X$),

E_a^b can be calculated as,

$$\Delta H = E_a^f - E_a^b$$
$$\Rightarrow \quad E_a^b = E_a^f - \Delta H$$
$$= 30 - (-20)$$
$$= 50\ kJ\ mol^{-1}$$

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68 The rate constant of a reaction increases by five times on increase in temperature from 27°C to 52°C. The value of activation energy in kJ mol^{-1} is ..... (Rounded off to the nearest integer)

[$R = 8.314\ J\ K^{-1}\ mol^{-1}$]

[2021, 25 Feb Shift-II]

Ans. ***(52)***

$T_1 = (273 + 27) = 300\ K$,

$T_2 = (273 + 52) = 325\ K$

Given, temperature coefficient of the reaction,

$$\alpha_T = \frac{K_{325}}{K_{300}} = 5$$

$$\log\frac{K_{T_2}}{K_{T_1}} = \frac{E_a}{2.303R}\times\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log\frac{K_{325}}{K_{300}} = \frac{E_a}{2.303\times 8.314}\left(\frac{325-300}{300\times 325}\right)$$

$$\log 5 = \frac{E_a}{2.303\times 8.319}\times\frac{25}{300\times 325}$$

$$E_a = 52194.78\ J\ mol^{-}$$

$$= 52.194\ kJ\ mol^{-1}$$

$$\simeq 52\ kJ\ mol^{-1}$$

69 The number of molecules with energy greater than the threshold energy for a reaction increases five fold by a rise of temperature from 27 °C to 42 °C. Its energy of activation in J/mol is ..... .

(Take $\ln 5 = 1.6094$; $R = 8.314\ J\ mol^{-1}\ K^{-1}$)

[2020, 4 Sep Shift-II]

Ans. ***(84297.47)***

Given, temperature rise 27°C to 42°C

Hence, $T_1 = 273 + 27 = 300\ K$

$T_2 = 273 + 42 = 315\ K$

$\{\ln 5 = 1.6094\ R = 8.314\ J\ mol^{-1}K^{-1}\}$

According to question $k_{T_2} = 5k_{T_1}$ as molecules activated are increased five times so k will increases 5 times. Now, $k = Ae^{-E_a/RT}$ (Arrhenius equation)

On apply log both sides

$$\ln\left(\frac{k_{T_2}}{k_{T_1}}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Here, $\frac{k_{T_2}}{k_{T_1}} = 5$

$$\ln 5 = \frac{E_a}{R}\left(\frac{1}{300} - \frac{1}{315}\right)$$

$$\ln 5 = \frac{E_a}{8.314}\left(\frac{315-300}{300\times 315}\right)$$

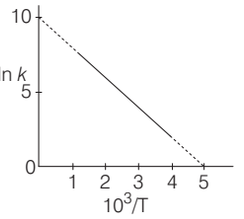
$$\ln 5 = \frac{E_a}{8.314}\times\frac{15}{300\times 315}$$

$$1.6094 = \frac{E_a}{8.314}\times\frac{15}{300\times 315}$$

$$E_a = \frac{1.6094\times 8.314\times 300\times 315}{15}$$

$$E_a = 84297.47\ 50\ J/mol$$

70 The rate constant (k) of a reaction is measured at different temperature (T), and the data are plotted in the given figure. The activation energy of the reaction in kJ mol^{-1} is (R is gas constant)



[2020, 5 Sep Shift-II]

(a) $\frac{2}{R}$ (b) $\frac{1}{R}$ (c) R (d) $2R$

Ans. ***(d)***

$\therefore \quad k = Ae^{-E_a/RT}$

Taking natural logarithm on both sides, the Arrhenius equation becomes.

$$\Rightarrow \quad \ln k = \ln A - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

$$\Rightarrow \quad \ln k = \ln A - \left(\frac{E_a}{R\times 10^3}\right)\times\frac{10^3}{T}$$

$$\text{Slope of a graph} = \frac{-E_a}{R\times 10^3} = \frac{-10}{5}$$

$$E_a = 2R\times 10^3\ J\ mol^{-1} \Rightarrow E_a = 2R\ kJ$$

71 The rate of a reaction decreased by 3.555 times when the temperature was changed from 40° C to 30° C. The activation energy (in kJ mol^{-1}) of the reaction is ..... .

(Take; $R = 8.314\ J\ mol^{-1}K^{-1}$, ln 3.555 = 1.268) **[2020, 6 Sep Shift-II]**

Ans. ***(100.00)***

The Arrhenius eqaution is

$$\ln\left(\frac{KT_2}{KT_1}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Given, $\frac{KT_2}{KT_1} = 3.555$

$R = 8.314\ JK^{-1}\ mol^{-1}$

$T_1 = 30 + 273 = 303\ K$; $T_2 = 40 + 273 = 313\ K$

Substituting the given values in the Arrhenius equation,

$$\ln(3.555) = \frac{E_a}{8.314}\left[\frac{1}{303} - \frac{1}{313}\right]$$

$(\ln 3.555 = 1.268)$

$$1.268 = \frac{E_a}{8.314}\left[\frac{313-303}{303\times 313}\right]$$

$$E_a = \frac{1.268\times 8.314\times 303\times 313}{10}$$

$$= 99980.7 = 99.98\ kJ/mol$$

72 The rate of a certain biochemical reaction at physiological temperature (T) occurs 10^6 times faster with enzyme than without. The change in the activation energy upon adding enzyme is :

[2020, 8 Jan Shift-I]

(a) $+ 6RT$ (b) $- 6(2.303)RT$

(c) $+ 6(2.303)RT$ (d) $- 6RT$

Ans. ***(b)***

Let the activation energy with and without enzyme be E_a^* and E_a.

Rate constant of reaction without catalyst is given by Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

Taking log on both sides, we get

$$\log k = \log A - \frac{E_a}{RT(2.303)} \quad ...(i)$$

With catalyst, rate constant is 10^6 times more

$$\therefore \quad 10^6 k = Ae^{\frac{-E_a}{RT}}$$

$$\log k + \log 10^6 = \log A - \frac{E_a^*}{RT(2.303)}$$

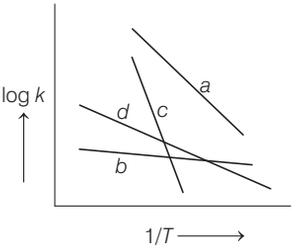
$$\therefore \quad \log k = \log A - \frac{E_a^*}{RT(2.303)} - 6 \quad ...(ii)$$

Comparing Eqs. (i) and (ii)

$$\frac{E_a}{RT(2.303)} = \frac{E_a^*}{RT(2.303)} + 6$$

$$\therefore \quad E_a^* - E_a = -6(2.303)RT$$

73 Consider the following plots of rate constant *versus* $\frac{1}{T}$ for four different reactions. Which of the following orders is correct for the activation energies of these reactions?



[2020, 8 Jan Shift-II]

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(a) $E_b > E_a > E_d > E_c$
(b) $E_a > E_c > E_d > E_b$
(c) $E_b > E_d > E_c > E_a$
(d) $E_c > E_a > E_d > E_b$

Ans. ***(d)***

According to Arrhenius equation

$$k = Ae^{-E_a/RT}$$

$$\Rightarrow \log k = \log A - \frac{E_{act}}{2.303RT}$$

E_{act} = activation energy

Slope of the graph of $\log K$ vs $\frac{1}{T}$ is $\frac{-E_{act}}{2.303R}$

Greater the value of E_{act}, more will be the negative slope.

From the graph,

most –ve slope = c, followed by a, d and b.

$\therefore$ Order of activation energies must be

$$E_c > E_a > E_d > E_b$$

74 For following reactions :

$$A \xrightarrow{700K} \text{Product};$$

$$A \xrightarrow[\text{Catalyst}]{500K} \text{Product}$$

It was found that the E_a is decreased by 30 kJ/mol in the presence of catalyst. If the rate remains unchanged, the activation energy for catalysed reaction is (Assume pre exponential factor is same): **[2020, 9 Jan Shift-I]**

(a) 198 kJ/mol (b) 105 kJ/mol
(c) 75 kJ/mol (d) 135 kJ/mol

Ans. ***(c)***

For catalysed reaction, let E_a be x.

Then, for uncatalysed reaction,

$E_a = x + 30$ (given in question).

Also, rate of reaction at 700 K (without catalyst) = rate of reaction at 500 K (with catalyst).

$\therefore k$ at 700 K without catalyst = k at 500 K with catalyst.

Using relation,

$$k = Ae^{-E_a/RT}$$

E_a = Activation energy.

$$\therefore \quad Ae^{-(x+30)/700R} = Ae^{-x/500R}$$

$$\therefore \quad \frac{x+30}{700} = \frac{x}{500}$$

$$\Rightarrow \quad 7x = 5x + 150$$

$$2x = 150$$

$$\Rightarrow \quad x = 75 \text{ kJ mol}^{-1}$$

75 A sample of milk splits after 60 min. at 300 K and after 40 min. at 400 K when the population of *lactobacillus acidophilus* in it doubles. The activation energy (in kJ/mol) for this process is closest to (Given, $R = 8.3 \text{ J mol}^{-1}\text{K}^{-1}$ $\ln\left(\frac{2}{3}\right) = 0.4$, $e^{-3} = 4.0$)

[2020, 9 Jan Shift-II]

Ans. ***(3.98)***

Time taken for milk to split $\propto \frac{1}{k}$

where, k = rate constant of the process and, k at 2 different temperatures and activation energy are related.

$$\ln\frac{k_2}{k_1} = \frac{-E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \ln\frac{t_1}{t_2}$$

$$\therefore \ln\left(\frac{60}{40}\right) = \frac{-E_a}{8.3}\left(\frac{1}{400} - \frac{1}{300}\right)$$

$$E_a = 0.4 \times 8.3 \times 1200$$

$$= 3984 \text{ J mol}^{-1} = 3.984 \text{ kJ mol}^{-1}$$

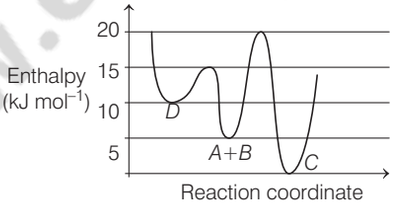
Given, $\ln\frac{2}{3} = 0.4 \Rightarrow \ln\frac{3}{2} = -0.4$

(These are wrong values, because $\ln\frac{2}{3}$ is –ve and $\ln\frac{3}{2}$ is +ve, but assume them to be correct).

76 Consider the given plot of enthalpy of the following reaction between A and B. $A + B \longrightarrow C + D$

Identify the incorrect statement.

[2019, 9 April Shift-II]

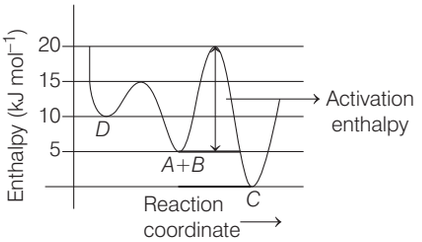


(a) D is kinetically stable product.
(b) Formation of A and B from C has highest enthalpy of activation.
(c) C is the thermodynamically stable product.
(d) Activation enthalpy to form C is 5 kJ mol^{-1} less than that to form D.

Ans. ***(d)***

Only statement (d) is incorrect.

Corrected statement is "Activation enthalpy to form C is 15 kg mol^{-1} more than 5 kg mol^{-1} that is required to form D." It can be easily explained by following graph.



Activation enthalpy (or energy) is the extra energy required by the reactant molecules that result into effective collision between them to form the products.

77 For the reaction of H_2 with I_2, the rate constant is $2.5 \times 10^{-4} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ at 327°C and $1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 527°C. The activation energy for the reaction, in kJ mol^{-1} is ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

[2019, 10 April Shift-II]

(a) 59 (b) 72
(c) 150 (d) 166

Ans. ***(d)***

Key Idea The Arrhenius equation for rate constants at two different temperatures is

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \quad [\text{where}, T_2 > T_1]$$

where, k_1 and k_2 are rate constants at temperatures T_1 and T_2, respectively.

R = Gas constant, E_a = Activation energy

For the reaction, $H_2 + I_2 \longrightarrow 2HI$

Given $k_1 = 2.5 \times 10^{-4} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$

$T_1 = (273 + 327) \text{ K} = 600 \text{ K}$

$k_2 = 1 \text{ dm}^3\text{mol}^{-1} \text{ s}^{-1}$

at $T_2 = (273 + 527) \text{ K} = 800 \text{ K}$

Now, $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

$$\Rightarrow \log\frac{1}{2.5 \times 10^{-4}} = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}}\left(\frac{800 - 600}{600 \times 800}\right)$$

$$\Rightarrow \log\frac{(10 \times 10^3)}{2.5} = \frac{E_a}{0.019} \times \frac{200}{48 \times 10^4}$$

$$\Rightarrow \log 4 + 3\log 10 \simeq E_a \times 0.022$$

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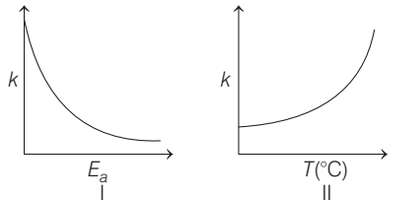
$$\Rightarrow \quad E_a = \frac{2\times\log 2 + 3}{0.022}$$
$$= \frac{3.6}{0.022} \simeq 163.6\ \text{kJ mol}^{-1}$$

78 Consider the given plots for a reaction obeying Arrhenius equation ($0°C < T < 300°C$) : (k and E_a are rate constant and activation energy, respectively)



Choose the correct option.

[2019, 10 Jan Shift-I]

(a) Both I and II are wrong
(b) Both I and II are correct
(c) I is wrong but II is right
(d) I is right but II is wrong

Ans. ***(b)***

The Arrhenius equation is, $k = A.e^{-E_a/RT}$

where, k = rate constant,

A = Arrhenius constant,

E_a = activation energy,

and T = temperature in K

From the equation, it is clear that k decreases exponentially with E_a . So, the plot-I is correct.

In the plot-II, k is plotted with temperature (in °C but not in K). So, at 0°C, $k \neq 0$ and k will increase exponentially with temperature upto 300°C. Therefore, the plot-II is also correct.

79 If a reaction follows the Arrhenius equation, the plot ln$k$ *vs* $1/(RT)$ gives straight line with a gradient ($-y$) unit.
The energy required to activate the reactant is **[2019, 11 Jan Shift-I]**

(a) $\frac{y}{R}$ unit (b) $-y$ unit
(c) yR unit (d) y unit

Ans. ***(d)***

The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation as,

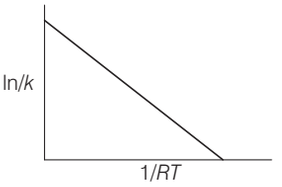
$$k = Ae^{-E_\alpha/RT} \qquad ...(i)$$

where, A = Arrhenius factor or frequency factor or pre-exponential factor

R = Gas constant,

E_a = Activation energy

Taking log on both sides of the Eq. (i), the equation becomes $\ln k = \ln A - \frac{E_a}{RT}$



On comparing with equation of straight line
($y = mx + c$), the nature of the plot of ln$k$ *vs* $\frac{1}{RT}$ will be :

(i) Intercept = $C = \ln A$

(ii) Slope/gradient = $m = -E_a = -y$
$\Rightarrow E_a = y$

So, the energy required to activate the reactant, (activation energy of the reaction, E_a is = y)

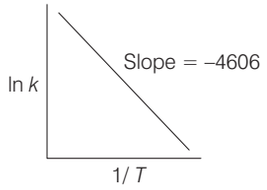
On comparing with equation of straight line
($y = mx + c$), the nature of the plot of ln$k$ *vs* $\frac{1}{RT}$ will be:

(i) Intercept = $C = \ln A$

(ii) Slope/gradient = $m = -E_a = -y$
$\Rightarrow E_a = y$

So, the energy required to activate the reactant, (activation energy of the reaction, E_a is = y)

80 For a reaction, consider the plot of ln k *versus* $1/T$ given in the figure. If the rate constant of this reaction at 400 K is 10^{-5} s^{-1}, then the rate constant at 500 K is



(a) 4×10^{-4} s^{-1}
(b) 10^{-6} s^{-1}
(c) 10^{-4} s^{-1}
(d) 2×10^{-4} s^{-1} **[2019, 12 Jan Shift-II]**

Ans. ***(c)***

The temperature dependence of a chemical reaction is expressed by Arrhenius equation,

$$k = Ae^{-E_a/RT} \qquad ...(i)$$

Taking natural logarithm on both sides, the Arrhenius equation becomes,

$$\ln k = \ln A - \frac{E_a}{RT}$$

where, $-\frac{E_a}{R}$ is the slope of the plot and ln$A$ gives the intercept.

Eq. (i) at two different temperatures for a reaction becomes,

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad ...(ii)$$

$\Rightarrow$ In the given problem,

$T_1 = 400$ K, $T_2 = 500$ K,

$k_1 = 10^{-5}$ s^{-1}, $k_2 = ?$

$-\frac{E_a}{R}$ (Slope) $= -4606$

On substituting all the given values in Eq. (ii), we get

$$\ln\frac{k_2}{10^{-5}} = 4606\left(\frac{1}{400} - \frac{1}{500}\right)$$
$$\ln\frac{k_2}{10^{-5}} = 2.303$$
$$\frac{k_2}{10^{-5}} = 10$$
$$\Rightarrow \quad k_2 = 10^{-4}\ s^{-1}$$

Therefore, rate constant for the reaction at 500 K is 10^{-4} s^{-1}.

81 Two reactions R_1 and R_2 have identical preexponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2, respectively at 300 K, then $\ln\left(\frac{k_2}{k_1}\right)$ is equal to ($R = 8.314$ J mol^{-1} K^{-1}) **[JEE Main 2017]**

(a) 8 (b) 12
(c) 6 (d) 4

Ans. ***(d)***

According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

where, A = collision number or pre-exponential factor.

R = gas constant,

T = absolute temperature

E_a = energy of activation

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For reaction R_1, $k_1 = Ae^{-E_{a_1}/RT}$ ...(i)

For reaction R_2, $k_2 = Ae^{-E_{a_2}/RT}$ ...(ii)

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{k_2}{k_1} = e^{-\frac{(E_{a_2} - E_{a_1})}{RT}} \quad ...(iii)$$

[$\because$ Pre-exponential factor 'A' is same for both reactions]

Taking ln on both the sides of Eq. (iii), we get

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_{a_1} - E_{a_2}}{RT}$$

Given, $E_{a_1} = E_{a_2} + 10\ \text{kJ mol}^{-1}$

$= E_{a_2} + 10{,}000\ \text{J mol}^{-1}$

$$\therefore \ln\frac{k_2}{k_1} = \frac{10{,}000\ \text{J mol}^{-1}}{8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300\ \text{K}} = 4$$

82 Higher order (>3) reactions are rare due to **[JEE Main 2015]**

(a) low probability of simultaneous collision of all the reacting species
(b) increase in entropy and activation energy as more molecules are involved
(c) shifting of equilibrium towards reactants due to elastic collisions
(d) loss of active species on collision

Ans. ***(a)***

The main conditions for the occurrence of a reaction is proper orientation and effective collision of the reactants. Since the chances of simultaneous collision with proper orientation between more than 3 species is very rare, so reaction with order greater than 3 are rare.

83 The rate of a reaction double when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be ($R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$ and $\log 2 = 0.301$) **[JEE Main 2013]**

(a) 53.6 kJ mol^{-1} (b) 48.6 kJ mol^{-1}
(c) 58.5 kJ mol^{-1} (d) 60.5 kJ mol^{-1}

Ans. ***(a)***

From Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{-E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Given, $\frac{k_2}{k_1} = 2; T_2 = 310\ \text{K} \Rightarrow T_1 = 300\ \text{K}$

On putting values,

$$\Rightarrow \log 2 = \frac{-E_a}{2.303 \times 8.314}\left(\frac{1}{310} - \frac{1}{300}\right)$$

$$\Rightarrow \quad E_a = 53603.93\ \text{J/mol} = 53.6\ \text{kJ/mol}$$

84 The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about **[AIEEE 2011]**

(a) 10 times (b) 24 times
(c) 32 times (d) 64 times

Ans. ***(c)***

For every 10°C rise of temperature, rate is doubled. Thus, temperature coefficient of the reaction = 2

When temperature is increased by 50°, rate becomes

$= 2^{(50/10)}$

$= 2^5$ times

$= 32$ times

85 A reactant (A) forms two products

$A \xrightarrow{k_1} B$, Activation energy E_{a_1}

$A \xrightarrow{k_2} C$, Activation energy E_{a_2}

If $E_{a_2} = 2E_{a_1}$, then k_1 and k_2 are related as **[AIEEE 2011]**

(a) $k_1 = 2k_2\, e^{E_{a_2}/RT}$

(b) $k_1 = k_2\, e^{E_{a_1}/RT}$

(c) $k_2 = k_1\, e^{E_{a_2}/RT}$

(d) $k_1 = Ak_2\, e^{E_{a_1}/RT}$

Ans. ***(b)***

$$A \xrightarrow{k_1} B,\ A \xrightarrow{k_2} C,$$

By Arrhenius equation,

$$k_1 = A' e^{-E_{a_1}/RT}$$

and $k_2 = A' e^{-E_{a_2}/RT}$. [A' is Arrhenius constant]

$\because \quad E_{a_2} = 2E_{a_1}$

$$\Rightarrow \quad k_2 = A' e^{-2E_{a_1}/RT}$$

$$\frac{k_1}{k_2} = \frac{A' e^{-E_{a_1}/RT}}{A' e^{-2E_{a_1}/RT}} = e^{E_{a_1}/RT}$$

$$\therefore \quad k_1 = k_2\, e^{E_{a_1}/RT}$$

86 The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1}, respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1}) **[AIEEE 2007]**

(a) 300 (b) 120
(c) 280 (d) 20

Ans. ***(d)***

$A_2 + B_2 \rightleftharpoons 2AB$

E_a (forward) = 180 kJ mol^{-1}

E_a (backward) = 200 kJ mol^{-1}

In the presence of catalyst,

E_a (forward) = 180 – 100

= 80 kJ mol^{-1}

E_a (backward) = 200 – 100

= 100 kJ mol^{-1}

$\Delta H = E_a$ (forward) – E_a (backward)

= 80 – 100

= – 20 kJ mol^{-1}

For the value of enthalpy change of the reaction, negative sign can be neglected.

87 Rate of a reaction can be expressed by Arrhenius equation as $k = Ae^{-E/RT}$

In this equation, E represents **[AIEEE 2006]**

(a) the energy above which all the colliding molecules will react
(b) the energy below which colliding molecules will not react
(c) the total energy of the reacting molecules at a temperature, T
(d) the fraction of molecules with energy greater than the activation energy of the reaction

Ans. ***(b)***

According to Arrhenius equation

$$k = Ae^{-E/RT}$$

where, E is the activation energy below which the colliding molecules will not react.

88 Consider an endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions respectively. In general **[AIEEE 2005]**

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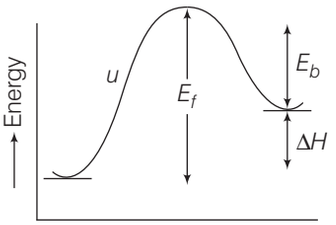
(a) there is no definite relation between E_b and E_f
(b) $E_b = E_f$
(c) $E_b > E_f$
(d) $E_b < E_f$

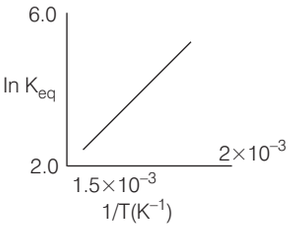
Ans. ***(d)***

$X \rightarrow Y$ is an endothermic reaction,
$\Delta H = +$ ve



E_b = energy of activation of backward reaction
E_f = energy of activation of forward reaction
ΔH = heat of reaction
Thus, $E_f = E_b + \Delta H$, $E_f > E_b$

89 A schematic plot of $\ln K_{eq}$ *versus* inverse of temperature for a reaction is shown below



The reaction must be **[AIEEE 2005]**

(a) highly spontaneous at ordinary temperature
(b) one with negligible enthalpy change
(c) endothermic
(d) exothermic

Ans. ***(d)***

Variation of K_{eq} with temperature T is given by van't Hoff equation.

$$\log K_{eq} = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{R}$$
$$\qquad\qquad A \qquad\quad B$$

Slope of the given line is positive indicating that term A is positive, thus ΔH° is negative.
Thus, reaction is exothermic.

90 In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statements is correct ? **[AIEEE 2003]**

(a) k is equilibrium constant
(b) A is adsorption factor
(c) E_a is energy of activation
(d) R is Rydberg constant

Ans. ***(c)***

By Arrhenius equation,
$k = Ae^{-E_a/RT}$,
k = Rate constant
A = Pre-exponential, frequency factor
E_a = Activation energy,
R = Gas constant
T = Temperature

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12

Surface Chemistry

TOPIC 1
Adsorption and Various Isotherms

01 CH_4 is adsorbed on 1 g charcoal at 0°C following the Freundlich adsorption isotherm. 10.0 mL of CH_4 is adsorbed at 100 mm of Hg, whereas 15.0 mL is adsorbed at 200 mm of Hg. The volume of CH_4 adsorbed at 300 mm of Hg is 10^x mL. The value of x is ..... $\times 10^{-2}$. (Nearest integer)

[Use $\log_{10} 2 = 0.3010$, $\log_{10} 3 = 0.4771$] **[2021, 31 Aug Shift-II]**

Ans. ***(128)***

According to Freundlich isotherm,

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

(Using, amount of adsorbate $\propto$ Volume of absorbate)

$$\frac{10}{1} = k \times (100)^{\frac{1}{n}} \quad ...(i)$$

$$\frac{15}{1} = k \times (200)^{\frac{1}{n}} \quad ...(ii)$$

$$\frac{v}{1} = k \times (300)^{\frac{1}{n}} \quad ...(iii)$$

Divide Eq. (ii) by (i)

$$\frac{15}{10} = 2^{\frac{1}{x}} \Rightarrow \log\left(\frac{3}{2}\right) = \frac{1}{n}\log 2$$

$$\frac{1}{n} = \frac{\log 3 - \log 2}{\log 2} = \frac{0.4771 - 0.3010}{0.3010}$$

$$\frac{1}{n} = 0.585$$

Divide Eq. (iii) by (i)

$$\frac{v}{10} = 3^{\frac{1}{n}}$$

$$\log\left(\frac{v}{10}\right) = \frac{1}{n}\log 3$$

$$\log\left(\frac{v}{10}\right) = 0.585 \times 0.4771 = 0.2791$$

$$\frac{v}{10} = 10^{0.2791}$$

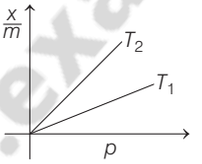
$$\Rightarrow \quad v = 10 \times 10^{0.2791}$$

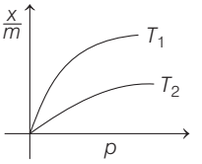
$$= 10^{1.279} = 10^x$$

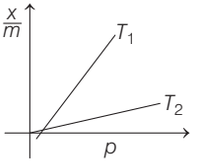
$$x = 1.279$$

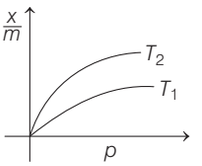
$$x = 128 \times 10^{-2}$$

02 Select the graph that correctly describes the adsorption isotherms at two temperatures T_1 and T_2 ($T_1 > T_2$) for a gas.
(x = mass of the gas adsorbed ; m = mass of adsorbent ; p = pressure) **[2021, 31 Aug Shift-I]**

(a) 

(b) 

(c) 

(d) 

Ans. ***(d)***

The graph that correctly describes the absorption isotherms at two temperature T_1 and T_2 is given by option (d).

According to Freundlich's adsorption isotherm, the amount of the gas adsorbed is directly proportional to pressure applied raised to the power $\frac{1}{n}$.

$$\frac{x}{m} \propto p^{\frac{1}{n}} \qquad \left[0 < \frac{1}{n} < 1\right]$$

So, on increasing temperature, $\frac{x}{m}$ decreases.

∴ Adsorption is basically exothermic in nature. Hence, correct option is (d).

03 Given below are two statement : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) $SO_2(g)$ is adsorbed to a large extent than $H_2(g)$ on activated charcoal.

Reason (R) $SO_2(g)$ has a higher critical temperature than $H_2(g)$.

In the light of the above statements, choose the most appropriate answer from the options given below. **[2021, 27 July Shift-II]**

(a) Both A and R are correct but R is not the correct explanation of A
(b) Both A and R are correct and R is the correct explanation of A.
(c) A is not correct but R is correct.
(d) A is correct but R is not correct.

Ans. ***(b)***

As intermolecular force of attraction increases, critical temperature increases. with increase in critical temperature, extent of adsorption also increases. As SO_2 has more critical

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temperature than H_2, it is adsorbed to a larger extent on charcoal.

∴Both Assertion and Reason are correct and Reason is the correct explanation for Assertion.

04 CO_2 gas adsorbs on charcoal following Freundlich adsorption isotherm. For a given amount of charcoal, the mass of CO_2 adsorbed becomes 64 times when the pressure of CO_2 is doubled. The value of n in the Freundlich isotherm equation is ..... $\times 10^{-2}$. (Round off to the nearest integer) **[2021, 27 July Shift-I]**

Ans. ***(17)***

According to Freundlich adsorption isotherm,

$$\frac{x}{m} = kp^{1/n}.$$

where x, m, k, p and n are amount of adsorbate, amount of adsorbent, pressure of gas and constant respectively.

For a given amount of charcoal, $x \propto p^{1/n}$

$$\frac{x_2}{x_1} = \left(\frac{p_2}{p_1}\right)^{1/n}$$

Therefore, $64 = (2)^{1/n}$

$$2^6 = 2^{1/n}$$

$$6 = \frac{1}{n}$$

$\Rightarrow$ $n = 0.166 = 0.17$

$$n = 17 \times 10^{-2}$$

05 Which one of the following is correct for the adsorption of a gas at a given temperature on a solid surface? **[2021, 26 Aug Shift-I]**

(a) $\Delta H > 0, \Delta S > 0$ (b) $\Delta H > 0, \Delta S < 0$

(c) $\Delta H < 0, \Delta S < 0$ (d) $\Delta H < 0, \Delta S > 0$

Ans. ***(c)***

The ΔH (enthalpy change) and ΔS (entropy change) will be less than zero for adsorption of gas on solid surface, i.e. $\Delta H < 0$, $\Delta S < 0$.

Entropy change (ΔS) The randomness of the gas molecules decreases as they are adsorb on solid surface due to restriction in their motion.

∴ ΔS is negative.

Enthalpy change (ΔH) Adsorption of gas on solid surface is an exothermic process, as there is force of attraction between adsorbate and adsorbent.

∴ΔH is negative.

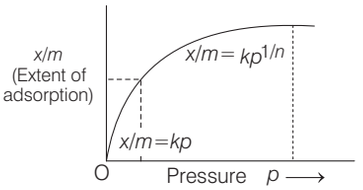
06 In Freundlich adsorption isotherm at moderate pressure, the extent of adsorption $\left(\frac{x}{m}\right)$ is directly proportional to p^x. The value of x is **[2021, 25 Feb Shift-I]**

(a) 1 (b) zero (c) ∞ (d) $\frac{1}{n}$

Ans. ***(d)***

According to Freundlich isotherm, at moderate pressure, extent of adsorption

$$\left(\frac{x}{m}\right) \propto (p)^{\frac{1}{n}}$$



At moderate pressure,

$$\frac{x}{m} = k(p)^{1/n}$$

$$\frac{x}{m} \propto (p)^{1/n} \quad \ldots(i)$$

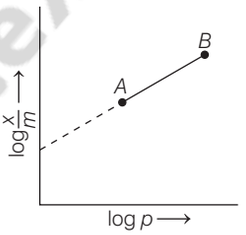
$$\frac{x}{m} \propto p^x \quad \text{(Given in question)} \ldots(ii)$$

Compare Eqs. (i) and (ii),

$$(p)^{1/n} \propto p^x$$

$$\therefore \quad x = \frac{1}{n}$$

07 In Freundlich adsorption isotherm, slope of AB line is **[2021, 24 Feb Shift-I]**



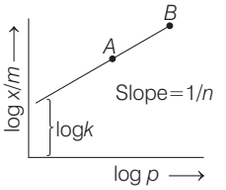
(a) n with ($n = 0.1$ to 0.5)

(b) $\log n$ with ($n > 1$)

(c) $\log \frac{1}{n}$ with ($n < 1$)

(d) $\frac{1}{n}$ with $\left(\frac{1}{n} = 0 \text{ to } 1\right)$

Ans. ***(d)***



Given graph is Freundlich adsorption isotherm.

According to equation,

$$\frac{x}{m} = kp^{\frac{1}{n}} \quad \ldots(i)$$

where, $\frac{x}{m}$ = amount of gas

k and n = constants depending upon nature of adsorbate and absorbent.

Now, taking log both side in Eq. (i), we get

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

For straight line, comparing above equation to $y = mx + c$

So, m = slope $= \frac{1}{n}$

hence, $0 \le \frac{1}{n} \le 1$

It value lies in between 0 to 1.

Hence, $\frac{1}{n}$ with $\left(\frac{1}{n} = 0 \text{ to } 1\right)$.

08 Amongst the following statements regarding adsorption, those that are valid are: **[2020, 2 Sep Shift-II]**

(A) ΔH becomes less negative as adsorption proceeds.

(B) On a given adsorbent, ammonia is adsorbed more than nitrogen gas.

(C) On adsorption, the residual force acting along the surface of the adsorbent increases.

(D) With increase in temperature, the equilibrium concentration of adsorbate increases.

(a) (D) and (A) (b) (B) and (C)

(c) (A) and (B) (d) (C) and (D)

Ans. ***(c)***

On adsorption (both physical and chemical), the residual force acting along the surface of absorbent decreases. So, ΔH of the adsorption becomes less negative as adsorption proceeds. So, statement (a) is correct but statement (c) is incorrect. Ammonia molecules (NH_3) is larger in size and dipolar in nature. Nitrogen is smaller in size and it is a non-polar molecule. So, degree of adsorption : $NH_3 > N_2$. So, statement (b) is correct. With increase in temperature, kinetic energy of adsorbate molecules will increase and hence, its equilibrium concentration will decrease.

So, statement (d) is not correct.

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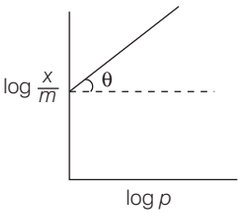
09 The mass of gas adsorbed, x per unit mass of adsorbate, m was measured at various pressures, p. A graph between $\log \frac{x}{m}$ and $\log p$ gives a straight line with slope equal to 2 and the intercept equal to 0.4771. The value of $\frac{x}{m}$ at a pressure of 4 atm is
(Given, log 3 = 0.4771)
[2020, 2 Sep Shift-I]

Ans. ***(6)***

From Freundlich adsorption isotherm equation,

$$\log \frac{x}{m} = \log K + \frac{1}{n}\log p$$



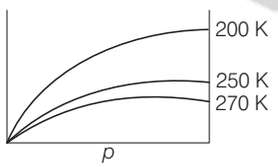
When we plot $\log x/m$ vs $\log p$, we get a straight line of

(i) $\text{slope} = \frac{1}{n} = 2 \Rightarrow n = \frac{1}{2}$

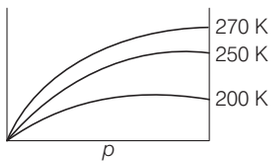
(ii) $\text{intercept} = \log K = 0.4771$
$\Rightarrow \log K = \log 3$
$\Rightarrow \quad K = 3$
So, $\frac{x}{m} = Kp^{1/n} = 3 \times 4^2$
$= 48.00 \quad (\because p = 4\,\text{atm})$

10 Adsorption of a gas follows Freundlich adsorption isotherm. If x is the mass of the gas adsorbed on mass m of the adsorbent, the correct plot of $\frac{x}{m}$ *versus* p is
[2020, 5 Sep Shift-II]

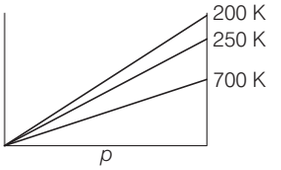
(a) $\frac{x}{m}$



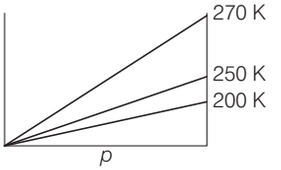
(b) $\frac{x}{m}$



(c) $\frac{x}{m}$

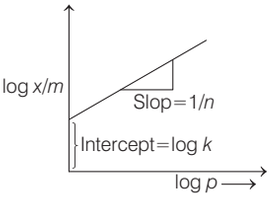


(d) $\frac{x}{m}$



Ans. ***(a)***

Freundlich adsorption gives the variation in the quantity of gas adsorbed by a unit mass of solid adsorbent with the change in pressure of the system for a given temperature.



The expression for the Freundlich isotherm can be represented by the following equation.

$$\frac{x}{m} = kp^{1/n}$$

where, $n > 1$

where, x is the mass of gas adsorbed, x is the mass of adsorbent. p is pressure and n is a constant, which depends upon the nature of adsorbent and the gas at a given temperature.

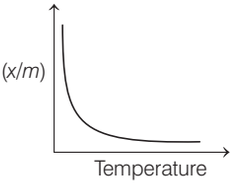
Taking the logarithm on both side of the equation,

$$\log \frac{x}{m} = \log k + \frac{1}{n}\log p$$

$\frac{x}{m} \propto p$ (At low pressure)

$\frac{x}{m} \propto p^0$ (At high pressure)

On increasing temperature physical adsorption decreases



Hence, option (a) is correct.

11 For Freundlich adsorption isotherm, a plot of $\log\left(\frac{x}{m}\right)$ (y-axis) and $\log p$ (x-axis) gives a straight line. The intercept and slope for the line is 0.4771 and 2, respectively. The mass of gas, adsorbed per gram of adsorbent if the initial pressure is 0.04 atm, is ..... $\times 10^{-4}$ g. ($\log 3 = 0.4771$)
[2020, 6 Sep Shift-II]

Ans. ***(48)***

According to Freundlich adsorption isotherm

$$\frac{x}{m} = Kp^{1/n} \quad \ldots(i)$$

Taking logarithm of Eq. (i)

$$\log \frac{x}{m} = \log K + \frac{1}{n}\log p \quad \ldots(ii)$$

Here, given slope $= \frac{1}{n} = 2$,

pressure (p) = 0.04 atm and intercept

$= \log K = 0.4771 \quad (\therefore K = 3)$

mass of gas adsorbed per gram of adsorbent

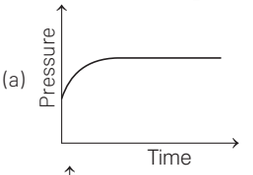
$$= \frac{x}{m} = K \cdot p^{1/n}$$

$$\frac{x}{m} = 3.p^2$$

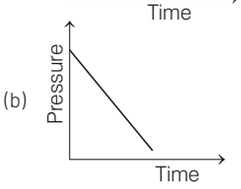
$\Rightarrow \quad \frac{x}{m} = 3 \times (0.04)^2 = 48 \times 10^{-4}$.

12 A mixture of gases O_2, H_2 and CO are taken in a closed vessel containing charcoal. The graph that represents the correct behaviour of pressure with time is
[2020, 9 Jan Shift-II]

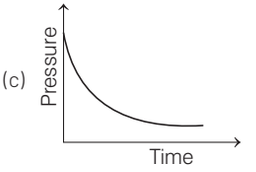
(a)



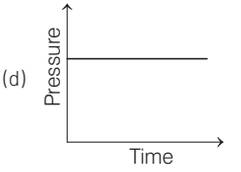
(b)



(c)



(d)



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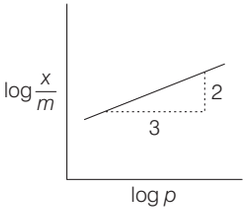
Ans. ***(c)***

Option (c) is the graph that represents correct behaviour of pressure with time. With passage of time, the pressure of the gases decreases and finally reach a constant value.

It is due to adsorption of gases by charcoal. The decrease in pressure is faster in the beginning, but as the adsorbent charcoal gets saturated, pressure attains constancy.

13 Adsorption of a gas follows Freundlich adsorption isotherm. x is the mass of the gas adsorbed on mass m of the adsorbent. The plot of $\log\frac{x}{m}$ *versus* $\log p$ is shown in the given graph. $\frac{x}{m}$ is proportional to

[2019, 8 April Shift-I]



(a) $p^{2/3}$ (b) $p^{3/2}$
(c) p^3 (d) p^2

Ans. ***(a)***

Key Idea According to Freundlich,

$$\frac{x}{m} = kp^{1/n}\ [n > 1]$$

where, m = mass of adsorbent, x = mass of the gas adsorbed, $\frac{x}{m}$ = amount of gas adsorbed per unit mass of solid adsorbent,
p = pressure, K and n = constants.

The logarithm equation of Freundlich adsorption isotherm is

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log p$$

On comparing the above equation with straight line equation, $(y = mx + c)$

we get $m = \text{slope} = \frac{1}{n}$ and $c = \log K$

From the given plot,

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{1}{n} = \frac{2}{3}$$

$$\Rightarrow \quad \frac{x}{m} = Kp^{2/3}$$

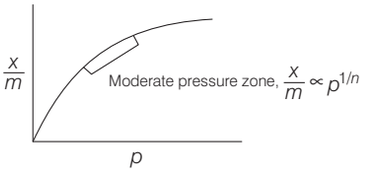
14 A gas undergoes physical adsorption on a surface and follows the given Freundlich adsorption isotherm equation $\frac{x}{m} = Kp^{0.5}$

Adsorption of the gas increases with **[2019, 10 April Shift-I]**

(a) increase in p and increase in T
(b) increase in p and decrease in T
(c) decrease in p and decrease in T
(d) decrease in p and increase in T

Ans. ***(b)***

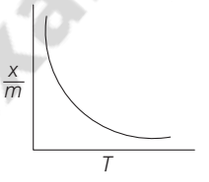
For physisorption or physical adsorption, Adsorption isotherm (Temperature, T = constant) is shown below:



where, x = amount of adsorbate,
m = amount of adsorbent,
$\frac{x}{m}$ = degree of adsorption
$\frac{1}{n}$ = order of the reaction, where, $0 < \frac{1}{n} < 1$
and so, $1 < n < \infty$

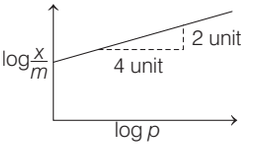
Here, $\frac{x}{m} = Kp^{\frac{1}{2}}$, i.e. $\frac{x}{m} \propto p^{\frac{1}{2}}$

Adsorption isobar (Pressure, p = constant)



So, the rate of physical adsorption of the gas, increases with p (when, T is constant) and decreases with T (when p is constant).

15 Adsorption of a gas follows Freundlich adsorption isotherm. In the given plot, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p. (x/m) is proportional to



(a) p^2 (b) $p^{1/4}$ (c) $p^{1/2}$ (d) p

[2019, 9 Jan Shift-I]

Ans. ***(c)***

According to Freundlich adsorption isotherm,

$$\frac{x}{m} \propto p^{\frac{1}{n}} \Rightarrow \frac{x}{m} = Kp^{1/n}$$

On taking log on both sides, we get

$$\log\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log p$$

On comparing with equation of straight line, $y = mx + c$, plot of $\log\frac{x}{m}$ vs $\log p$ gives,

Slope $\frac{(y_2 - y_1)}{(x_2 - x_1)} = \frac{1}{n} \Rightarrow \frac{2}{4} = \frac{1}{2}$

$$\Rightarrow \quad \frac{x}{m} \propto p^{1/2}$$

16 The correct match between item-I and Item-II is

A. Benzaldehyde
P. Dynamic phase
B. Alumina
Q. Adsorbent
C. Acetonitrile
R. Adsorbate **[2019, 9 Jan Shift-II]**

(a) (A) → (R); (B) → (Q); (C) → (P)
(b) (A) → (P); (B) → (R); (C) → (Q)
(c) (A) → (Q); (B) → (P); (C) → (R)
(d) (A) → (Q); (B) → (R); (C) → (P)

Ans. ***(a)***

Using the principle of adsorption chromatography, qualitative and quantitative analysis of benzaldehyde can be done from its mixture with acetonitrile. Here, a mobile phase moves over a stationary phase (adsorbent). Adsorbents used are alumina (Al_2O_3) and silica gel. The sample solution of benzaldehyde and acetonitrile when comes in contact with the adsorbent, benzaldehyde gets adsorbed on the surface of the adsorbent. So, benzaldehyde acts as absorbate whereas acetonitrile starts moving as mobile phase over the stationary phase of the adsorbate. Hence, act as dynamic phase.

17 Given,

Gas :	H_2,	CH_4,	CO_2,	SO_2
Critical temp./K	33	190	304	630

On the basis of data given above, predict which of the following gases shows least adsorption on a definite amount of charcoal?

(a) CH_4 (b) SO_2 (c) CO_2 (d) H_2

[2019, 12 Jan Shift-I]

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Ans. ***(d)***

Same adsorbant (charcoal in this case) at same temperature will adsorb different gases to different extent. The extent to which gases are adsorbed is proportional to the critical temperature of gas.

$\because \quad T_c = \frac{8a}{27Rb}$

where, a is the magnitude of intermolecular forces between gaseous molecules.

Thus, higher the cirtical temperature more is the gas adsorbed. Among the given gases, H_2 has the minimum critical temperature, i.e. 33K thus, it shows least adsorption on a definite amount of charcoal.

18 For a linear plot of $\log(x/m)$ *versus* $\log p$ in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants) **[JEE Main 2016]**

(a) $1/n$ appears as the intercept

(b) Only $1/n$ appears as the slope

(c) $\log\left(\frac{1}{n}\right)$ appears as the intercept

(d) Both k and $1/n$ appear in the slope term

Ans. ***(b)***

According to Freundlich adsorption isotherm,

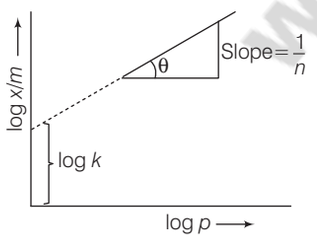
$$\frac{x}{m} = kp^{1/n}$$

On taking logarithm of both sides, we get

$$\log\frac{x}{m} = \log k + \log p^{1/n}$$

or $$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

$$y = c + mx$$



$y = \log\frac{x}{m}$, c = intercept = $\log k$,

m = slope = $\frac{1}{n}$

and $x = \log p$

19 According to Freundlich adsorption isotherm which of the following is correct? **[AIEEE 2012]**

(a) $\frac{x}{m} \propto p^0$

(b) $\frac{x}{m} \propto p^1$

(c) $\frac{x}{m} \propto p^{1/n}$

(d) All of the above are correct for different range of pressure

Ans. ***(d)***

By Freundlich adsorption isotherm

$$\frac{x}{m} = kp^{1/n}$$

[In between low and high pressure range]

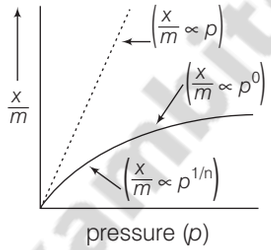
When $n = 1$,

$$\frac{x}{m} \propto p^1$$

[In low pressure range]

When n is large, $\frac{x}{m} = k$

[Independent of pressure]



Thus, $\frac{x}{m} \propto p^0$

[At high pressure range when saturation point is reached]

20 Which of the following statements is incorrect regarding physisorptions? **[AIEEE 2009]**

(a) It occurs because of van der Waals' forces

(b) More easily liquefiable gases are adsorbed readily

(c) Under high pressure, it results into multi molecular layer on adsorbent surface

(d) Enthalpy of adsorption ($\Delta H_{adsorption}$) is slow and positive

Ans. ***(d)***

Adsorption is an exothermic process *i.e.*, energy is released against van der Waals' force of attraction (physisorptions).

Hence, ΔH is always negative.

21 In Langmuir's model of adsorption of a gas on a solid surface **[AIEEE 2006]**

(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered

(b) the adsorption at a single site on the surface may involve multiple molecules at the same time

(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas

(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

Ans. ***(c)***

The adsorption of a gas is directly proportional to the pressure of the gas.

22 Which one of the following characteristics is not correct for physical adsorption? **[AIEEE 2003]**

(a) Adsorption on solids is reversible

(b) Adsorption increases with increase in temperature

(c) Adsorption is spontaneous

(d) Both enthalpy and entropy of adsorption are negative

Ans. ***(b)***

As temperature increases desorption increases. Adsorbent + Adsorbate $\rightleftharpoons$ Adsorbed state + ΔE

Adsorption is exothermic process (forward direction), desorption is endothermic process (backward direction).

According to Le-Chatelier's principle, increase in temperature favours endothermic process.

TOPIC 2
Catalyst

23 Which one of the following statements is not true about enzymes ? **[2021, 20 July Shift-II]**

(a) Enzymes are non-specific for a reaction and substrate.

(b) Almost all enzymes are proteins.

(c) Enzymes work as catalysts by lowering the activation energy of a biochemical reaction.

(d) The action of enzymes is temperature and pH specific.

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Ans. ***(a)***

Statement (a) is not true whereas all other statements are true.

An enzyme is a substance that acts as a catalyst in living organism, regulating rate at which chemical reaction proceed without itself being altered in the process.

The biological processes that occur within all living organisms are chemical reaction and most are regulated by enzymes. Enzymes are highly specific in nature.

24 Match List-I with List-II.

	List-I (Process)		List-II (Catalyst)
(A)	Deacon's process	(i)	ZSM-5
(B)	Contact process	(ii)	$CuCl_2$
(C)	Cracking of hydrocarbons	(iii)	Particles 'Ni'
(D)	Hydrogenation of vegetable oils	(iv)	V_2O_5

Choose the most appropriate answer from the options given below **[2021, 18 March Shift-I]**

	A	B	C	D		A	B	C	D
(a)	(ii)	(iv)	(i)	(iii)	(b)	(i)	(iii)	(ii)	(iv)
(c)	(iii)	(i)	(iv)	(ii)	(d)	(iv)	(ii)	(i)	(iii)

Ans. ***(a)***

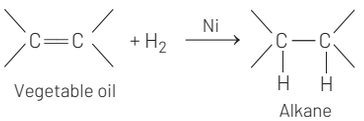
A. Deacon's process is used for industrial preparation of chlorine gas.

$$HCl + [O_2] \xrightarrow[723\,K]{CuCl_2} H_2O + Cl_2$$

B. Contact process is used for industrial preparation of sulphuric acid where V_2O_5 as a catalyst involved in the process.

C. ZSM-5 used as catalyst in cracking of hydrocarbons.

D. Ni catalysts enables the hydrogenation of fats.



Vegetable oil — Alkane

∴ Correct match is (A-ii), (B-iv), (C-i), (D-iii).

25 For the following Assertion and Reason the correct option is

Assertion For hydrogenation reactions, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity shown by Group 7-9 elements.

Reason The reactants are most strongly adsorbed on group 7-9 elements. **[2020, 8 Jan Shift-II]**

(a) The Assertion is true, but the Reason is false.

(b) Both Assertion and Reason are true, but the Reason is not the correct explanation for the Assertion.

(c) Both Assertion and Reason are true and the Reason is the correct explanation for the Assertion.

(d) Both Assertion and Reason are false.

Ans. ***(a)***

Assertion is correct but Reason is incorrect. Correct reason is as follows: To show maximum catalytic activity, reactants must be adsorbed on to the surface of catalysis reasonably strong but not too strong to become immobilised. So, most catalytic activity corresponds to a moderately strong adsorption, not extremely strong adsorption.

26 Match the catalysts Column I with products Column II.

	Column I (Catalyst)		Column II (Product)
(A)	V_2O_5	(i)	Polyethlyene
(B)	$TiCl_4 / Al(Me)_3$	(ii)	Ethanal
(C)	$PbCl_2$	(iii)	H_2SO_4
(D)	Iron oxide	(iv)	NH_3

[2019, 9 April Shift-I]

(a) (A)-(ii), (B)-(iii), (C)-(i), (D)-(iv)

(b) (A)-(iv), (B)-(iii), (C)-(ii), (D)-(i)

(c) (A)-(iii), (B)-(i), (C)-(ii), (D)-(iv)

(d) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)

Ans. ***(c)***

Correct match is

(A) → (iii); (B) → (i); (C) → (ii); (D) → (iv)

(i) $TiCl_4 + AlCl_3$ (*Ziegler- Natta* catalyst) is used to prepare polyethylene from ethene.

(ii) V_2O_5 (Vanadium pentoxide) is used as catalyst to prepare H_2SO_4 from contact process. Reaction involved is

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

It is the key step in the manufacture of H_2SO_4.

(iii) Fe (Iron) is used as catalyst in Haber's process for the manufacture of ammonia.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

(iv) Pd (Palladium) is used to prepare ethanal. Reaction involved is

$$H_2C{=}{=}CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2 / CuCl_2} CH_3CHO$$

This reaction is also known as Wacker's process.

27 Which of the following is not an example of heterogeneous catalytic reaction?

(a) Haber's process

(b) Combustion of coal

(c) Hydrogenation of vegetable oils

(d) Ostwald's process **[2019, 10 Jan Shift-I]**

Ans. ***(b)***

In heterogeneous catalytic reactions, physical state of reactants and that of catalyst(s) used are different.

Haber's process, hydrogenation of vegetable oils and Ostwald's process all are heterogeneous process. Combustion of coal is not a heterogeneous catalytic reaction.

In Haber's process

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s),\ Mo(s)} 2NH_3(g)$$

Hydrogenation of vegetable oils,

$$\underset{\text{(Unsaturated)}}{\text{Vegetable oil(l)}} \xrightarrow[\text{or Ni}(s)]{[(Ph_3P)_3Rh]Cl} \underset{\text{Vanaspat (s)}}{}$$

Ostwald's process,

$$4NH_3(g) + 5O_2(g) \xrightarrow[V_2O_5(s)]{Pt(s)} 4NO(g) + 6H_2O(g)$$

No catalyst is used in combustion of coal. The reaction is highly spontaneous in nature.

$$\underset{\text{(Coal)}}{C} + O_2 \longrightarrow CO_2$$

28 Match the catalysts to the correct processes. **[JEE Main 2015]**

	Catalyst		Process
(A)	$TiCl_3$	(i)	Wacker process
(B)	$PdCl_2$	(ii)	Ziegler- Natta polymerisation
(C)	$CuCl_2$	(iii)	Contact process
(D)	V_2O_5	(iv)	Deacon's process

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(a) (A)-(iii), (B)-(ii), (C)-(iv), (D)-(i)
(b) (A)-(ii), (B)-(i), (C)-(iv), (D)-(iii)
(c) (A)-(ii), (B)-(iii), (C)-(iv), (D)-(i)
(d) (A)-(iii), (B)-(i), (C)-(ii), (D)-(iv)

Ans. ***(b)***

(a) $TiCl_3$ is used as Ziegler-Natta catalyst for the polymerisation of ethene.
(b) $PdCl_2$ is used in Wacker process, in which alkene changed into aldehyde *via* catalytic cyclic process initiated by $PdCl_2$.
(c) $CuCl_2$ is used in Deacon's process. (for Cl_2)
(d) V_2O_5 is used in contact process of manufacturing sulphuric acid.

Time Saving Technique This type of questions can also be solved through elimination technique. There is no need to know all the four matches to select the correct response. Even if you know (b) matches then also you can solve the problem. e.g. suppose you know the usage of V_2O_5 in contact process (i.e. D matches with (iii) and $TiCl_3$ is connected to Ziegler-Natta catalyst (i.e. A matches with ii).

These two combinations are present only in option number (b). Likewise, for this question particularly if you know that V_2O_5 is used in contact process then this combination is present in option (b) only out of all the four option given. In this way you can eliminate wrong options to get the correct response.

TOPIC 3
Colloids, Micelles and Emulsions

29 Match List-I with List-II.

List-I (Colloid preparation method)	**List-II** (Chemical reaction)
A. Hydrolysis	1. $2AuCl_3 + 3HCHO + 3H_2O \rightarrow 2Au(sol) + 3HCOOH + 6HCl$
B. Reduction	2. $As_2O_3 + 3H_2S \rightarrow As_2S_3(sol) + 3H_2O$
C. Oxidation	3. $SO_2 + 2H_2S \rightarrow 3S(sol) + 2H_2O$
D. Double Decomposition	4. $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3(sol) + 3HCl$

Choose the most appropriate answer from the options given below. **[2021, 1 Sep Shift-II]**

	A	B	C	D		A	B	C	D
(a)	1	3	2	4	(b)	4	1	3	2
(c)	4	2	3	1	(d)	1	2	4	3

Ans. ***(b)***

According to type of reaction for colloid preparation, colloids have been classified.

A. Hydrolysis –
$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3(sol) + 3HCl$

B. Reduction–
$2AuCl_3 + 3HCHO + 3H_2O \longrightarrow 2Au(sol) + 3HCOOH + 6HCl$

C. Oxidation– $SO_2 + 2H_2S \longrightarrow 3S(sol) + 2H_2O$

D. Double decomposition–
$As_2O_3 + 3H_2S \longrightarrow As_2S_3(sol) + 3H_2O$

Hence, the correct match is
$A \rightarrow 4, B \rightarrow 1, C \rightarrow 3, D \rightarrow 2.$

30 Lyophilic sols are more stable than lyophobic sols because **[2021, 27 Aug Shift-II]**

(a) there is a strong electrostatic repulsion between the negatively charged colloidal particles.
(b) the colloidal particles have positive charge.
(c) the colloidal particles have no charge.
(d) the colloidal particles are solvated.

Ans. ***(d)***

Lyophilic sols are more stable than lyophobic sols. Lyophilic sols are solvent loving, whereas lyophobic sols are solvent hating. The dispersed phase in lyophobic sols has no attraction for the solvent. The dispersed phase in lyophilic sols has attraction for the solvent. The colloidal particles are solvated in the dispersed medium and therefore stabilised through solvation process. Therefore, the option (d) is correct.

31 The conditions given below are in the context of observing Tyndall effect in colloidal solutions

(A) The diameter of the colloidal particles is comparable to the wavelength of light used.
(B) The diameter of the colloidal particles is much smaller than the wavelength of light used.
(C) The diameter of the colloidal particles is much larger than the wavelength of light used.
(D) The refractive indices of the dispersed phase and the dispersion medium are comparable.
(E) The dispersed phase has a very different refractive index from the dispersion medium.

Choose the most appropriate conditions from the options given below. **[2021, 20 July Shift-I]**

(a) (A) and (E) only
(b) (C) and (D) only
(c) (A) and (D) only
(d) (B) and (E) only

Ans. ***(a)***

Option (*A*) and (*E*) are the conditions for showing Tyndall effect in colloidal solution.

The phenomenon of scattering of light by colloidal particles as a result of which the path of the beam becomes visible is called a Tyndall effect. Smaller the diameter and similar the magnitude of refractive indices, lesser is the scattering and hence the Tyndall effect. The diameter of the dispersed phase particle should not be smaller than the wavelength of light used because they won't be able to scatter the light so, therefore, the diameter of the dispersed particles should be equal or not much smaller than the wavelength of the light used.

In option (D), the refractive index (i.e. the ratio of the velocity of light in vacuum to the velocity of light in any medium) of the dispersed phase and the dispersion medium should differ greatly in magnitude then only the particles will be able to scatter the light and Tyndall effect will be observed.

Hence, option (a) is correct.

32 Tyndall effect is more effectively shown by **[2021, 27 Aug Shift-I]**

(a) true solution
(b) lyophilic colloid
(c) lyophobic colloid
(d) suspension

Ans. ***(c)***

Tyndall effect is more effectively shown by lyophobic colloid because in lyophobic colloids, the particles are not as highly solvated as in lyophilic sols. So, the

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difference in refractive index between the particles and the medium is quite large in lyophobic colloids. Therefore, the tyndall effect is more pronounced in lyophobic sols or colloids.

33 The sol given below with negatively charged colloidal particles is **[2021, 26 Aug Shift-II]**

(a) $FeCl_3$ added to hot water
(b) KI added to $AgNO_3$ solution
(c) $AgNO_3$ added to KI solution
(d) $Al_2O_3 \cdot xH_2O$ in water

Ans. *(c)*

- When $AgNO_3$ is added to KI,

$$KI \xrightarrow{AgNO_3} AgI\downarrow \xrightarrow{KI} \underset{\text{Negatively charged}}{AgI\ I^-}$$

Iodide ion gets adsorbed on the surface of AgI. This will result in formation of negatively charged colloids.

- When KI is added to $AgNO_3$ following reaction takes place.

$$AgNO_3 \xrightarrow{KI} AgI\downarrow \xrightarrow{AgNO_3} \underset{\text{Positively charged}}{AgI\ Ag^+}$$

Silver cation gets adsorbed on surface of AgI, resulting in formation of positively charged colloids.

- Option (a) and (d) will form positively charged colloids.

34 Match List I with List II.

	List I		List II
(A)	Cheese	I.	Dispersion of liquid in liquid
(B)	Pumice stone	II.	Dispersion of liquid in gas
(C)	Hair cream	III.	Dispersion of gas in solid
(D)	Cloud	IV.	Dispersion of liquid in solid

Choose the most appropriate answer from the options given below. **[2021, 25 July Shift-II]**

	A	B	C	D
(a)	IV	III	II	I
(b)	IV	I	III	II
(c)	III	IV	I	II
(d)	IV	III	I	II

Ans. *(d)*

Dispersion of various system in which distributed particles of one material are dispersed in a continuous phase of another material. The two phases may be in the same or different state of matter.

Cheese → Dispersion of liquid in solid.

Pumice stone → Dispersion of gas in solid.

Hair cream → Dispersion of liquid in liquid.

Cloud → Dispersion of liquid in gas.

35 100 mL of 0.0018% (*w*/*v*) solution of Cl^- ion was the minimum concentration of Cl^- required to precipitate a negative sol in one h. The coagulating value of Cl^- ion is ..... (Nearest integer) **[2021, 20 July Shift-II]**

Ans. *(1)*

Coagulation value The minimum concentration of electrolyte in millimoles required to cause coagulation of 1 L of colloidal solution.

Given, 0.0018 g Cl^- present in 100 mL solution

Coagulation value of Cl^- is

$$= \frac{\frac{0.0018}{35.5} \times 10^3}{0.1} = 0.5070 \simeq 1$$

36 The charges on the colloidal CdS sol and TiO_2 sol are, respectively **[2021, 18 March Shift-II]**

(a) positive and positive
(b) positive and negative
(c) negative and negative
(d) negative and positive

Ans. *(d)*

Oxides and hydroxide sol are positively charged.

So, TiO_2 is positive sol. Sulphide sol are negatively charge hence, CdS is negatively charge sol.

37 For the coagulation of a negative sol, the species below, that has the highest flocculating power is **[2021, 17 March Shift-II]**

(a) SO_4^{2-} (b) Ba^{2+}
(c) Na^+ (d) PO_4^{3-}

Ans. *(b)*

To coagulate negative sol, Ba^{2+} cation has highest coagulation value.

For a negative sol, a positive ion is required for flocculation.

According to Hardy-Schulze law, greater the valence of the flocculating ion added, the greater is its power to cause precipitation.

38 A colloidal system consisting of a gas dispersed in a solid is called a/an **[2021 , 17 March Shift-I]**

(a) solid sol (b) gel
(c) aerosol (d) foam

Ans. *(a)*

A colloidal system consisting of a gas (dispersed phase) dispersed in a solid (dispersed medium) is called a solid sol.

	DP	DM	Type of colloid
(a)	Gas	Solid	Solid sol
(b)	Liquid	Solid	Gel
(c)	Solid	Gas	Aerosol
(d)	Gas	Liquid	Foam

39 The nature of charge on resulting colloidal particles when $FeCl_3$ is added to excess of hot water is **[2021, 26 Feb Shift-II]**

(a) Positive
(b) Sometimes positive and sometimes negative
(c) Neutral
(d) Negative

Ans. *(a)*

When $FeCl_3$ is added to excess of hot water,
a positively charged hydrated ferric oxide $[Fe_2O_3 \cdot xH_2O/Fe^{3+}]$ is formed due to adsorption Fe^{3+} ion (adsorbate) on the surface of hydrated ferric oxide (adsorbent).

$$FeCl_3 \xrightarrow[\Delta]{H_2O(\text{Excess})} \underset{\substack{\text{(Positively charged sol}\\ \text{or positive colloid)}}}{[Fe_2O_3 \cdot xH_2O] \cdot Fe^{3+} + 3Cl^-(aq)}$$

40 Which one of the following statements is false for hydrophilic sols ? **[2021, 25 Feb Shift-II]**

(a) They do not require electrolytes for stability.
(b) These sols are reversible in nature.
(c) Their viscosity is of the order of that of H_2O.
(d) The sols cannot be easily coagulated.

Ans. *(c)*

Statement (c) is false whereas other statements are true. Corrected statement is as follows :

Viscosity of hydrophilic sols is higher than that of the dispersion medium, i.e. H_2O, because there is a high concentration of dispersed phase in water.

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41 Most suitable salt which can be used for efficient clotting of blood will be **[2021, 24 Feb Shift-II]**

(a) $NaHCO_3$ (b) $FeSO_4$
(c) $Mg(HCO_3)_2$ (d) $FeCl_3$

Ans. ***(d)***

According to Hardy-Schulze rule, for negatively charged sol, most (+ve) charged ion is needed for efficient coagulation.

Blood is a negatively charged sol. Hence $FeCl_3$ can be used for blood clotting and it from Fe^{3+} ion.

42 Tyndall effect is observed when **[2020, 3 Sep Shift-I]**

(a) the diameter of dispersed particles is much larger than the wavelength of light used
(b) the diameter of dispersed particles is much smaller than the wavelength of light used
(c) the refractive index of dispersed phase is greater than that of the dispersion medium
(d) the diameter of dispersed particles is similar to the wavelength of light used

Ans. ***(d)***

Tyndall effect, an optical property, is observed by colloids, preferably lyophobic colloidal sols.

Here, visible light of wavelength range more than 400 nm scattered when they are incident on colloidal particles of sizes (diameter, 10^{-7} - 10^{-5} cm) commensurate with their wavelengths. In lyophobic colloids, refractive index of the dispersed phase is smaller than that of dispersion medium.

So, option (c) is also not correct.

43 Match the following:

I. Foam	(A) Smoke
II. Gel	(B) Cell fluid
III. Aerosol	(C) Jellies
IV. Emulsion	(D) Rubber
	(E) Froth
	(F) Milk

[2020, 4 Sep Shift-I]

(a) (I)-(D), (II)-(B), (III)-(A), (IV)-(E)
(b) (I)-(B), (II)-(C), (III)-(E), (IV)-(D)
(c) (I)-(E), (II)-(C), (III)-(A), (IV)-(F)
(d) (I)-(D), (II)-(B), (III)-(E), (IV)-(F)

Ans. ***(c)***

Correct match is (I) → E, (II) → C, (III) → A, (IV) → F

(I) Foam – Froth
Foam forms gas particles trapped in solid or liquid.
(II) Gel – Jellies
Gel is a colloid, where dispersed phase is liquid and dispersion medium is solid.
(III) Aerosol – Smoke
Aerosol is a colloid, where solid/liquid particles dispersed in gas.
(IV) Emulsion– Milk
Emulsion is formed by mixing two liquids. (Milk is combination of 2 liquid)

44 A sample of red ink (a colloidal suspension) is prepared by mixing eosin dye, egg white, HCHO and water. The component which ensures stability of the ink sample is **[2020, 4 Sep Shift-II]**

(a) egg white (b) eosin dye
(c) HCHO (d) water

Ans. ***(a)***

Egg white is a lyophilic colloid and for its stability lyophobic colloid is mixed in it. Because, egg white is a lyophilic colloid it is mixed with red ink sample for its stability. Hence, option (a) is correct.

45 Which of the following is used for the preparation of colloids? **[2020, 2 Sep Shift-I]**

(a) Bredig's Arc method
(b) Ostwald process
(c) Mond process
(d) van Arkel method

Ans. ***(a)***

Using Bredig's arc method, colloids (metal sols which are lyophobic) can be prepared.

In this method, two electrodes of metal (whose sol is to be prepared) are dipped in concentrated alkali. The electrodes act as arc for high voltage transmission of current. The metal particles get dispersed in the medium to produce metal sols like Au-sol, Ag-sol, Pt-sol etc.

Ostwald process is an industrial process for manufacturing HNO_3. Reactions are as follows :

(i) $4NH_3 + 5O_2 \xrightarrow[500\ K,\ 9\ atm]{Pt\ gauge} 3NO + 6H_2O$

(ii) $2NO + O_2 \longrightarrow 2NO_2$

(iii) $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$

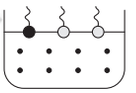
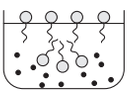
Mond process is associated with refining of nickel.

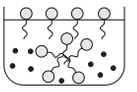
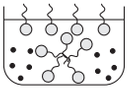
$$\underset{Crude}{Ni} + 4\,O \xrightarrow{80^\circ C} [Ni(CO)_4] \xrightarrow[-4\,CO]{200^\circ C} \underset{Pure}{Ni}$$

van Arkel method, ultra pure Zr, Hf, Ti metals get refined.

$$\underset{Crude}{Zr} + 4I_2 \xrightarrow{600^\circ C} ZrI_4(g) \xrightarrow[-2\,I_2]{1800^\circ C} \underset{Pure}{Zr}$$

46 Identify the correct molecular picture showing what happens at the critical micellar concentration (CMC) of an aqueous solution of a surfactant (• polar head; ~~ non-polar tail; • water). **[2020, 5 Sep Shift-I]**

(*A*)  (*B*) 

(*C*)  (*D*) 

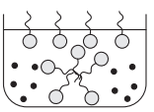
(a) (*C*) (b) (*B*)
(c) (*D*) (d) (*A*)

Ans. ***(d)***

CMC (critical micelle concentration) is the concentration of a surfactant in a bulk phase, above which aggregates of surfactant molecules, so called micelles, start to form.

A micelle is an aggregate of monomer surfactant molecules dispersed in a liquid colloid.

Hydrophilic 'Head' regions in contact with surrounding solvent, sequestering the hydrophobic 'Tail' regions in the micelle centre.



Hence, option (d) is correct.

47 Kraft temperature is the temperature **[2020, 6 Sep Shift-II]**

(a) below which the aqueous solution of detergents starts freezing
(b) below which the formation of micelles takes place
(c) above which the aqueous solution of detergents starts boiling
(d) above which the formation of micelles takes place

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Ans. ***(d)***

Micelles formation take place only above a particular temperature called Kraft temperature (T_K).

Hence, the correct option is (d).

48 The flocculation value of HCl for arsenic sulphide sol. is 30 m mol L^{-1}. If H_2SO_4 is used for the flocculation of arsenic sulphide, the amount in grams of H_2SO_4 is 250 mL required for the above purpose is ..... (molecular mass of H_2SO_4 = 98 g / mol)

[2020, 7 Jan Shift-II]

Ans. ***(0.37)***

(exact value : 0.3675 g)

Flocculation value = number of m mol of electrolyte needed per litre.

Since, As_2S_3 is negatively charged colloid, H^+ causes its flocculation.

Here, 30 m mol of HCl is needed per 1 L

per 250 mL, HCl required would be

$$= \frac{30 \times 250}{1000} = 7.5 \text{ m mol}$$

$\therefore n_{H^+}$ required = 7.5 m mol

So, mol of H_2SO_4 required $= \frac{7.5 \text{ m mol}}{2}$

$= 3.75$ m mol

Mass of $H_2SO_4 = \frac{3.75 \times 98}{1000} = 0.3675$ g.

The value may range from 0.36 to 0.38.

49 As per Hardy-Schulze formulation, the flocculation values of the following for ferric hydroxide sol are in the order : **[2020, 8 Jan Shift-I]**

(a) $K_3[Fe(CN)_6] < K_2CrO_4 < AlCl_3 < KBr < KNO_3$

(b) $AlCl_3 > K_3[Fe(CN_6] > K_2CrO_4 > KBr = KNO_3$

(c) $K_3[Fe(CN)_6] < K_2CrO_4 < KBr = KNO_3 = AlCl_3$

(d) $K_3[Fe(CN)_6] > AlCl_3 > K_2CrO_4 > KBr > KNO_3$

Ans. ***(c)***

Ferric hydroxide sol (and other metal oxide and hydroxide sols) is generally positively charged. So, as per Hardy-Schulze rule, the flocculation power is greatest for electrolyte having most highly negatively charged anion.

$\therefore$ Flocculation power follow the order

$$\underset{\text{Anionic charge : (-3)}}{K_3[Fe(CN)_6]} > \underset{(-2)}{K_2CrO_4} > \underset{(-1)}{KBr}$$

$= KNO_3 = AlCl_3$

As flocculation power increases, flocculation value decreases. Therefore, order of flocculation values is

$K_3[Fe(CN)_6] < K_2CrO_4 < KBr$

$= KNO_3 = AlCl_3$

50 The aerosol is a kind of colloid in which **[2019, 9 April Shift-I]**

(a) gas is dispersed in liquid

(b) gas is dispersed in solid

(c) liquid is dispersed in water

(d) solid is dispersed in gas

Ans. ***(d)***

The aerosol is a kind of colloid in which solid is dispersed in gas. e.g. smoke, dust.

51 The correct option among the following is **[2019, 10 April Shift-II]**

(a) colloidal medicines are more effective, because they have small surface area.

(b) brownian motion in colloidal solution is faster if the viscosity of the solution is very high.

(c) addition of alum to water makes it unfit for drinking.

(d) colloidal particles in lyophobic sols can be precipitated by electrophoresis.

Ans. ***(d)***

The explanation of the given statements are as follows :

(a) Colloidal medicines are more effective because they (dispersed phase) have larger surface area.

Thus, option (a) is incorrect.

(b) Brownian motion of dispersed phase particles in colloidal solution is faster if the viscosity of the solution is very low. Thus, option (b) is incorrect.

(c) Addition of alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$), an electrolyte to water makes it fit for drinking purposes because alum coagulates mud particles from water.

Thus, option (c) is incorrect.

(d) Precipitation of lyophobic solution particles by electrophoresis is called cottrell precipitation.

Thus, option (d) is correct.

52 Peptisation is a **[2019, 12 April Shift-I]**

(a) process of bringing colloidal molecule into solution

(b) process of converting precipitate into colloidal solution

(c) process of converting a colloidal solution into precipitate

(d) process of converting soluble particles to form colloidal solution

Ans. ***(b)***

Peptisation is a process of converting precipitate into colloidal solution. This process involves the shaking of precipitate with the dispersion medium in the presence of small amount of electrolyte. The electrolyte added is called peptising agent.

During peptisation, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately breakup into smaller particles of the size of a colloid.

53 Among the following, the incorrect statement about colloids is **[2019, 12 April Shift-II]**

(a) They can scatter light

(b) They are larger than small molecules and have high molar mass

(c) The osmotic pressure of a colloidal solution is of higher order than the true solution at the same concentration

(d) The range of diameters of colloidal particles is between 1 and 1000 nm

Ans. ***(c)***

Statement (c) is incorrect about colloids. Colligative properties such as relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure of a colloidal solution is of low order than the true solution at the same concentration.

54 Which of the salt-solution is most effective for coagulation of arsenious sulphide?

(a) $BaCl_2$ (b) $AlCl_3$ (c) Na_3PO_4 (d) NaCl

[2019, 9 Jan Shift-II]

Ans. ***(b)***

Arsenious sulphide sol is a negative colloid, $As_2S_3.(S^{2-})$. So, it will be coagulated by the cation of an electrolyte.

According to the Hardy-Schulze rule, the higher the charge of the ion, the more effective it is in bringing about coagulation. Here, the cations available are Al^{3+} (from $AlCl_3$), Ba^{2+} (from $BaCl_2$) and Na^+ (from Na_3PO_4 and NaCl). So, their power to coagulate $As_2S_3.(S^{2-})$ will follow the order as

$$Al^{3+} > Ba^{2+} > Na^+$$

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55 Haemoglobin and gold sol are examples of

(a) negatively and positively charged sols, respectively
(b) negatively charged sols
(c) positively charged sols
(d) positively and negatively charged sols, respectively

[2019, 10 Jan Shift-II]

Ans. ***(d)***

Haemoglobin and gold sol both are colloids and always carry an electric charge. Haemoglobin is a positively charged sol, because in haemoglobin, Fe^{2+} ion is the central metal ion of the octahedral complex.

All metal sols like, Au-sol, Ag-sol etc; are negatively charged sols.

56 An example of solid sol is

[2019, 11 Jan Shift-I]

(a) gem stones (b) hair cream
(c) butter (d) paint

Ans. ***(a)***

Solid sol consists of solid as both dispersed phase and dispersion medium. In gemstones, metal crystals (salt and oxides of metals) are dispersed in solid (stone) medium. Hair cream is an emulsion (liquid in liquid). Butter is a colloidal solution of liquid in solid. Paint is also sol (solid in liquid).

57 Among the colloids cheese (*C*), milk (*M*) and smoke (*S*), the correct combination of the dispersed phase and dispersion medium, respectively is **[2019, 11 Jan Shift-II]**

(a) *C* : liquid in solid; *M* : liquid in liquid; *S* : solid in gas
(b) *C* : solid in liquid; *M* : liquid in liquid; *S* : gas in solid
(c) *C* : liquid in solid; *M* : liquid in solid; *S* : solid in gas
(d) *C* : solid in liquid; *M* : solid in liquid; *S* : solid in gas

Ans. ***(a)***

Dispersed phase	Dispersion medium	Type of colloid	Examples
Liquid	Solid	Gel	Cheese (C), butter, jellies
Liquid	Liquid	Emulsion	Milk (M), hair cream
Solid	Gas	Aerosol	Smoke (S), dust

Thus, *C* : liquid in solid, *M* : liquid in liquid and *S* : solid in gas.

58 Among the following, the false statement is

(a) Tyndall effect can be used to distinguish between a colloidal solution and a true solution
(b) It is possible to cause artificial rain by throwing electrified sand carrying charge opposite to the one on clouds from an aeroplane
(c) Lyophilic sol can be coagulated by adding an electrolyte
(d) Latex is a colloidal solution of rubber particles which are positively charged

[2019, 12 Jan Shift-II]

Ans. ***(d)***

Statement given as statement (d) is incorrect. Latex is a stable dispersion, i.e. emulsion of polymer microparticles in an aqueous medium.

These microparticles belong to rubber and are negatively charged in nature. Natural latex contains some amount of sugar, resin, protein and ash as well.

The closest synthetic latex that can be associated with the properties of natural latex is SBR, i.e. Styro Butane Rubber.

Rest of all the statements are correct.

59 The Tyndall effect is observed only when following conditions are satisfied **[JEE Main 2017]**

I. The diameter of the dispersed particles is much smaller than the wavelength of the light used.
II. The diameter of the dispersed particle is not much smaller than the wavelength of the light used.
III. The refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude.
IV. The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.

(a) I and IV (b) II and IV
(c) I and III (d) II and III

Ans. ***(b)***

Colloidal solutions show Tyndall effect due to scattering of light by colloidal particles in all directions in space. It is observed only under the following conditions.

(i) The diameter of the colloids should not be much smaller than the wavelength of light used.
(ii) The refractive indices of the dispersed phase and dispersion medium should differ greatly in magnitude.

60 The coagulating power of electrolytes having ions Na^+, Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order **[JEE Main 2013]**

(a) $Al^{3+} < Ba^{2+} < Na^+$
(b) $Na^+ < Ba^{2+} < Al^{3+}$
(c) $Ba^{2+} < Na^{2+} < Al^{3+}$
(d) $Al^{3+} < Na^+ < Ba^{2+}$

Ans. ***(b)***

According to Hardy Schulze rule, greater the charge on oppositely charged ion, greater is its coagulating power. Since arsenic sulphide is a negatively charged sol, thus, the order of coagulating power is $Na^+ < Ba^{2+} < Al^{3+}$.

61 Gold numbers of protective colloids *A*, *B*, *C* and *D* are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is **[AIEEE 2008]**

(a) $D < A < C < B$
(b) $C < B < D < A$
(c) $A < C < B < D$
(d) $B < D < A < C$

Ans. ***(c)***

Higher the gold number, lesser will be the protective power of colloid.

62 The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statement is not correct?

(a) Coagulation in both sols can be brought about by electrophoresis
(b) Mixing the sols has no effect
(c) Sodium sulphate solution causes coagulation in both sols
(d) Magnesium chloride solution coagulates the gold sol more readily than the iron (III) hydroxide sol **[AIEEE 2005]**

Ans. ***(b)***

Mixing the sols together can cause coagulation, since the charges are neutralised.

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13

Classification of Elements and Periodicity in Properties

TOPIC 1

Periodic Table and Classification of Elements

01 Identify the element for which electronic configuration in +3 oxidation state is $[Ar]3d^5$.

[2021, 1 Sep Shift-II]

(a) Ru (b) Mn
(c) Co (d) Fe

Ans. ***(d)***

Iron (Fe) has electronic configuration $[Ar]3d^5$ in +3 oxidation state.

Electronic configuration of Fe
$= [Ar]3d^6, 4s^2$

Electronic configuration of
$Fe^{3+} = [Ar]3d^5$.

02 Outermost electronic configuration of a group-13 element E is $4s^2\,4p^1$. The electronic configuration of an element of p-block period-five placed diagonally to element, E is

[2021, 20 July Shift-II]

(a) $[Kr]3d^{10}4s^24p^2$
(b) $[Ar]3d^{10}4s^24p^2$
(c) $[Xe]5d^{10}6s^26p^2$
(d) $[Kr]4d^{10}5s^25p^2$

Ans. ***(d)***

	13th	14th	15th
2nd period $2s^22p^1$	B	C	N
3rd period $3s^23p^1$	Al	Si	P
4th period $4s^24p^1$	Ga	Ge	As
5th period $5s^25p^1$	In	Sn	Sb

That element is $_{50}Sn \Rightarrow [Kr]4d^{10}5s^25p^2$

03 The atomic number of the element unnilennium is **[2020, 3 Sep Shift-I]**

(a) 109 (b) 102
(c) 108 (d) 119

Ans. ***(a)***

The atomic number of the element unnilennium is 109.

(a) $Z = \underbrace{1}_{un}\ \underbrace{0}_{nil}\ \underbrace{9}_{enn} - ium \Rightarrow$ unnilennium

(b) $Z = \underbrace{1}_{un}\ \underbrace{0}_{nil}\ \underbrace{2}_{bi} - ium \Rightarrow$ unnilbiium

(c) $Z = \underbrace{1}_{un}\ \underbrace{1}_{nil}\ \underbrace{8}_{oct} - ium \Rightarrow$ unniloctium

(d) $Z = \underbrace{1}_{un}\ \underbrace{1}_{nil}\ \underbrace{9}_{enn} - ium \Rightarrow$ ununennium

Hence, option (a) is correct.

04 The process that is not endothermic in nature is

[2020, 4 Sep Shift-II]

(a) $O^-(g) + e^- \longrightarrow O^{2-}(g)$
(b) $Na(g) \longrightarrow Na^+(g) + e^-$
(c) $H(g) + e^- \longrightarrow H^-(g)$
(d) $Ar(g) + e^- \longrightarrow Ar^-(g)$

Ans. ***(c)***

(a) $O^-(g) + e^- \longrightarrow O^{2-}(g)$ (endothermic)
(b) $Na(g) \longrightarrow Na^+(g) + e^-$ (endothermic)
(c) $H(g) + e^- \longrightarrow H^-(g)$ (exothermic)
(d) $Ar(g) + e^- \longrightarrow Ar^-(g)$ (endothermic)

Reaction (c) is not endothermic. It is exotherrnic. Electron gain ethalpy of $H(g)$ is negative, due to 's' configuration while that of $Ar(g)$ is positive due to ns^2np^6 configuration.

Second election gain enthalpy is always positive for an atom.

Ionisation potential of an atom is positive.

05 The correct electronic configuration and spin-only magnetic moment (BM) of Gd^{3+} ($Z = 64$), respectively, are

[2020, 5 Sep Shift-I]

(a) $[Xe]4f^7$ and 7.9 (b) $[Xe]5f^7$ and 7.9
(c) $[Xe]5f^7$ and 8.9 (d) $[Xe]4f^7$ and 8.9

Ans. ***(a)***

Electronic configuration of Gd^{3+} is

$_{64}Gd^{3+} = [Xe]4f^7$

$= [Xe]$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

Gd^{3+} having 7 unpaired electrons.

Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

$\Rightarrow \quad \mu = \sqrt{7(7+2)}$ BM $= 7.9$ BM

where, n = number of unpaired electrons.

06 In the sixth period, the orbitals that are filled are **[2020, 5 Sep Shift-I]**

(a) $6s, 5f, 6d, 6p$ (b) $6s, 4f, 5d, 6p$
(c) $6s, 5d, 5f, 6p$ (d) $6s, 6p, 6d, 6f$

Ans. ***(b)***

Filling of electrons in orbitals in any period takes place as :

$$s \rightarrow \underset{\text{if possible}}{ns}\,(n-2)\underset{\text{if possible}}{f}\,(n-l)d\ np$$

$\therefore$ A per $(n+l)$ rule for sixth period $n = 6$, orbitals that are filled are

$6s$, $4f$, $5d$ and $6p$

07 The atomic number of unnilunium is ..... . **[2020, 6 Sep Shift-II]**

Ans. ***(101)***

Unnilunium

IUPAC symbol = Unu

Atomic number $(Z) = 101$

Because, the roots are strung together in the order of digits which makes up the

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atomic numbers and 'ium' is added at the end.

Digit	Name	Abbreviation
1	un`	u
0	nil	n
1	un	u

08 The electronic configuration of bivalent europium and trivalent cerium are
(atomic number : Xe = 54, Ce = 58 Eu = 63) **[2020, 9 Jan Shift-I]**
(a) $[Xe]4f^7$ and $[Xe]4f^1$
(b) $[Xe]4f^7 6s^2$ and $[Xe]4f^2 6s^2$
(c) $[Xe]4f^2$ and $[Xe]4f^7$
(d) $[Xe]4f^4$ and $[Xe]4f^9$

Ans. ***(a)***

The electronic configuration of bivalent europium and trivalent cerium are as follows:

$_{63}Eu = [Xe]4f^7 5d^0 6s^2 \Rightarrow Eu^{2+} = [Xe]4f^7$

$_{58}Ce = [Xe]4f^1 5d^1 6s^2 \Rightarrow Ce^{3+} = [Xe]4f^1$

09 The size of the iso-electronic species Cl^-, Ar and Ca^{2+} is affected by **[2019, 8 April Shift-I]**
(a) azimuthal quantum number of valence shell
(b) electron-electron interaction in the outer orbitals
(c) principal quantum number of valence shell
(d) nuclear charge

Ans. ***(d)***

The radius of isoelectronic species is inversely proportional to their nuclear charge or atomic number (Z). Thus, greater the value of Z, lesser the radii of isoelectronic species.

10 The IUPAC symbol for the element with atomic number 119 would be **[2019, 8 April Shift-II]**
(a) unh (b) uue
(c) uun (d) une

Ans. ***(b)***

Atomic number (119) = 1 (un) 1 (un) 9 (en)

So, symbol of the element = uue
Name of the element = ununennium
It is expected to be s-block element an alkali metal and the first element in eighth period. It is the lightest element that has not yet been synthesised.

11 The isoelectronic set of ions is **[2019, 10 April Shift-I]**
(a) F^-, Li^+, Na^+ and Mg^{2+}
(b) N^{3-}, Li^+, Mg^{2+} and O^{2-}
(c) Li^+, Na^+, O^{2-} and F^-
(d) N^{3-}, O^{2-}, F^- and Na^+

Ans. ***(d)***

Key Idea Isoelectronic species contains same number of electrons.

The species with its atomic number and number of electrons are as follows :

Species (ions)	At. no. (Z)	No. of electrons
N^{3-}	7	7 + 3 = 10
O^{2-}	8	8 + 2 = 10
F^-	9	9 + 1 = 10
Na^+	11	11 − 1 = 10
Li^+	3	3 − 1 = 2
Mg^{2+}	12	12 − 2 = 10

Thus, option (d) contains isoelectronic set of ions.

12 The group number, number of valence electrons and valency of an element with atomic number 15, respectively, are **[2019, 12 April Shift-I]**
(a) 16, 5 and 2 (b) 15, 5 and 3
(c) 16, 6 and 3 (d) 15, 6 and 2

Ans. ***(b)***

The group number, number of valence electrons and valency of an element with atomic number 15 are 15, 5 and 3 respectively. Modern periodic table is based on the atomic number. Number of valence electrons present in an atom decides the group number.

Electronic configuration of element having atomic number
$15 = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
(Valence electrons)

As five electrons are present in valence shell, its group number is 15. Valency of element having atomic number 15 is +3 (8 − 5 = 3).

13 The element with $Z = 120$ (not yet discovered) will be an/a **[2019, 12 Jan Shift-I]**
(a) transition metal
(b) inner-transition metal
(c) alkaline earth metal
(d) alkali metal

Ans. ***(c)***

The element with $Z = 120$ will be an alkaline earth metal. Recently, oganesson (Og) with atomic number 118 is named by IUPAC is a noble gas and placed just two place before 120. So, the general electronic configuration is represented as [noble gas] ns^2 and element with $Z = 120$ exist as an alkaline earth metal.

14 The group having isoelectronic species is **[JEE Main 2017]**
(a) O^{2-}, F^-, Na^+, Mg^{2+}
(b) O^-, F^-, Na, Mg^+
(c) O^{2-}, F^-, Na, Mg^{2+}
(d) O^-, F^-, Na^+, Mg^{2+}

Ans. ***(a)***

Isoelectronic species are those which contains same number of electrons.

Species	Atomic number	Number of electrons
O^{2-}	8	10
F^-	9	10
Na^+	11	10
Mg^{2+}	12	10
O^-	8	9
Na	11	11
Mg^+	12	11

∴ Option (a) is correct which contains isoelectronic species O^{2-}, F^-, Na^+, Mg^{2+}.

15 Which one of the following sets of ions represents a collection of isoelectronic species ? **[AIEEE 2006]**
(a) K^+, Cl^-, Ca^{2+}, Sc^{3+}
(b) Ba^{2+}, Sr^{2+}, K^+, S^{2-}
(c) N^{3-}, O^{2-}, F^-, S^{2-}
(d) Li^+, Na^+, Mg^{2+}, Ca^{2+}

Ans. ***(a)***

Isoelectronic means having same number of electrons,
K^+, Cl^-, Ca^{2+}, Sc^{3+} (all are having 18 electrons).

16 According to the periodic law of elements, the variation in properties of elements is related to their **[AIEEE 2003]**
(a) atomic masses
(b) nuclear masses
(c) atomic numbers
(d) nuclear neutron-proton number ratios

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Ans. *(c)*

All physical and chemical properties of elements are periodic function of their atomic number— Modern Periodic Law.

TOPIC 2
Periodic Properties

17 The correct order of ionic radii for the ions, $P^{3-}, S^{2-}, Ca^{2+}, K^{+}, Cl^{-}$ is **[2021, 27 Aug Shift-II]**

(a) $P^{3-} > S^{2-} > Cl^{-} > K^{+} > Ca^{2+}$
(b) $Cl^{-} > S^{2-} > P^{3-} > Ca^{2+} > K^{+}$
(c) $P^{3-} > S^{2-} > Cl^{-} > Ca^{2+} > K^{+}$
(d) $K^{+} > Ca^{2+} > P^{3-} > S^{2-} > Cl^{-}$

Ans. *(a)*

The electronic configuration of given ions are as follows :

K_{19} = 2, 8, 8, 1	K^{+} = 2, 8, 8
Ca_{20} = 2, 8, 8, 2	Ca^{2+} = 2, 8, 8
P_{15} = 2, 8, 5	P^{3-} = 2, 8, 8
S_{16} = 2, 8, 6	S^{2-} = 2, 8, 8
Cl_{17} = 2, 8, 7	Cl^{-} = 2, 8, 8

As the effective nuclear charge increases from P to Ca, the atomic size decreases in the same order.

Order of ionic radii

$$\underset{15}{P^{3-}} > \underset{16}{S^{2-}} > \underset{17}{Cl^{-}} > \underset{19}{K^{+}} > \underset{20}{Ca^{2+}}$$

Therefore, option (a) is correct.

18 Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Metallic character decreases and non-metallic character increases on moving from left to right in a period.

Reason (R) It is due to increase in ionisation enthalpy and decrease in electron gain enthalpy, when one moves from left to right in a period.

In the light of the above statements, choose the most appropriate answer from the options given below. **[2021, 31 Aug Shift-I]**

(a) (A) is false but (R) is true.
(b) (A) is true but (R) is false
(c) Both (A) and (R) are correct and (R) is the correct explanation of (A).
(d) Both (A) and (R) are correct but (R) is not the correct explanation of (A).

Ans. *(b)*

On moving from left to right in periodic table, metallic character decreases while non-metallic character increases. This is due to decrease in ionisation enthalpy and increase in electron gain enthalpy when we move from left to right in periodic table. Hence, (A) is true while (R) is false.

Hence, correct option is (b).

19 The correct order of first ionisation enthalpy is **[2021, 27 July Shift-II]**

(a) Mg < S < Al < P
(b) Mg < Al < S < P
(c) Al < Mg < S < P
(d) Mg < Al < P < S

Ans. *(c)*

The correct order of first ionisation enthalpy is Al < Mg < S < P.

Generally, it increases on moving from left to right in a period. But due to the presence of half-filled ($3s^2 3p^3$) orbital in P and fully filled ($3s^2$) in Mg, results in the high ionisation energy.

20 The ionic radii of F^{-} and O^{2-} respectively are 1.33 Å and 1.4 Å while the covalent radius of N is 0.74Å. The correct statement for the ionic radius of N^{3-} from the following is **[2021, 25 July Shift-II]**

(a) it is smaller than F^{-} and N
(b) it is bigger than O^{2-} and F^{-}
(c) it is bigger than F^{-} and N, but smaller than of O^{2-}
(d) it is smaller than O^{2-} and F^{-}, but bigger than of N

Ans. *(b)*

The electronic configuration of F^{-}, O_2^{-} and N^{3-} are given below.

$$\left.\begin{aligned} F^{-} &= 1s^2 2s^2 2p^6 \\ O^{2-} &= [He]\,2s^2 2p^6 \\ N^{3-} &= [He]\,2s^2 2p^6 \end{aligned}\right\} 10\ e^{-}$$

(isoelectronic species)

Among all these, N^{3-} have least number of protons due to which its size increases as least nuclear attractions experienced by outer shell electrons.

From top to bottom of periodic table ions will increase in radii. However, now left to right, the radius is more of a function of the number of proton or nuclear charge. Similarly, O^{2-} will be larger than F^{-} as both have 10 electrons but $Z = 8$ for oxygen and $Z = 9$ for fluorine.

∴ Option (b) is correct.

21 *AX* is a covalent diatomic molecule, where *A* and *X* are second row elements of periodic table. Based on molecular orbital theory, the bond order of *AX* is 2.5. The total number of electrons in *AX* is ..... . (Round off to the nearest integer). **[2021, 18 March Shift-I]**

Ans. *(15)*

AX is a covalent diatomic molecule. The molecule is NO (Nitric oxide). Its bond order is 2.5 and it has a total of 15 electrons (7 + 8 = 15).

Here 'A' denotes nitrogen (N) and 'X' denotes oxygen (O). NO is colourless and toxic gas.

Note : Total number of electrons equal to 13 will also have the 2.5 bond order, but in this case neutral diatomic molecule will not be possible.

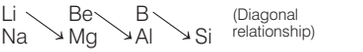
22 The set of elements that differ in mutual relationship from those of the other sets is **[2021, 17 March Shift-II]**

(a) Li-Mg (b) B-Si
(c) Be-Al (d) Li-Na

Ans. *(d)*

Li-Na pair is different from remaining three options as it do not shows diagonal relationship. Both Li-Na belongs to same group and are not placed diagonally.

Li - Mg, B - Si and Be - Al show diagonal relationship.



23 Identify the elements *X* and *Y* using the ionisation energy values given below.

	Ionisation energy (Ist)	**kJ/mol** (IInd)
X	495	4563
Y	731	1450

[2021, 16 March Shift-II]

(a) *X* = Na, *Y* = Mg
(b) *X* = Mg, *Y* = F
(c) *X* = Mg, *Y* = Na
(d) *X* = F, *Y* = Mg

Ans. *(a)*

Given data,

	IE_1	IE_2
X	495	4563 kJ/mol
Y	731	1450 kJ/mol

X is Na ($3s^1$) as it has very high second ionisation energy due to removal of

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electron from highly stable noble gas configuration.

$Na \xrightarrow{IE_1} Na^+ + e^-$; $IE_1 = 495$ kJ/mol

$1s^2 2s^2 2p^6 3s^1$ $1s^2 2s^2 2p^6$ or [Ne]

$Na^+ \xrightarrow{IE_2} Na^{2+} + e^-$; $IE_2 = 4563$ kJ/mol

$1s^2 2s^2 2p^6$ $1s^2 2s^2 2p^5$

(Stable noble gas configuration).

In case of Mg, noble gas configuration is achieved after removal of second electron. So, IE_2 is comparatively less.

$$\underset{[Ne]3s^2}{Mg} \longrightarrow \underset{[Ne]3s^1}{Mg^+} + e^-; \quad IE_1 = 731 \text{ kJ/mol}$$

$$\underset{[Ne]3s^1}{Mg^+} \longrightarrow \underset{[Ne]}{Mg^{2+}} + e^-; \quad IE_2 = 1450 \text{ kJ/mol}$$

24 The first ionisation energy of magnesium is smaller as compared to that of elements *X* and *Y*, but higher than that of *Z*. The elements *X*, *Y* and *Z*, respectively, are **[2021, 18 March Shift-II]**

(a) chlorine, lithium and sodium
(b) argon, lithium and sodium
(c) argon, chlorine and sodium
(d) neon, sodium and chlorine

Ans. ***(c)***

The order of first ionisation energy of 3rd period is as follows

Na < Al < Mg < Si < S < P < Cl<Ar

On moving along a period from left to right, nuclear charge increases that outweighs the shielding effect. As a result, outermost electrons are held more tightly. Hence, ionisation enthalpy increases.

Ionisation enthalpy of group 2 is greater than group 13 and that of group 15 is greater than group 16. This is due to fully filled and half-filled orbital.

∴ *X*, *Y* and *Z* are argon, chlorine and sodium respectively.

25 Which pair of oxides is acidic in nature? **[2021, 26 Feb Shift-II]**

(a) B_2O_3, CaO (b) B_2O_3, SiO_2
(c) N_2O, BaO (d) CaO, SiO_2

Ans. ***(b)***

(a) B_2O_3 ⟶ oxide of boron (non-metal) : acidic
CaO ⟶ oxide of calcium (metal) : basic

(b) B_2O_3 ⟶ oxide of boron (non-metal) : acidic
SiO_2 ⟶ oxide of silicon (non-metal) : acidic

(c) N_2O ⟶ oxide of nitrogen (non-metal) : neutral
BaO ⟶ oxide of barium (metal) : basic

(d) CaO ⟶ oxide of calcium (metal): basic
SiO_2 ⟶ oxide of silicon (non-metal): acidic

So, option (b) is the correct answer. B_2O_3 and SiO_2 are being acidic oxide they react with base to give salt and water.

$$B_2O_3 + 2NaOH \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + H_2O$$

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O$$

26 Match List-I with List-II.

	List-I (Electronic configuration of elements)		**List-II** (Δ_i in kJ mol^{-1})
A.	$1s^2 2s^2$	(i)	801
B.	$1s^2 2s^2 2p^4$	(ii)	899
C.	$1s^2 2s^2 2p^3$	(iii)	1314
D.	$1s^2 2s^2 2p^1$	(iv)	1402

Choose the most appropriate answer from the options given below. **[2021, 26 Feb Shift-I]**

A B C D
(a) (ii) (iii) (iv) (i)
(b) (i) (iv) (iii) (ii)
(c) (i) (iii) (iv) (ii)
(d) (iv) (i) (ii) (iii)

Ans. ***(a)***

Here, (B), (C) and (D) are *p*-block elements of the 2nd period.

(D) ⟶ p^1 configuration → B of group 13
(C) ⟶ p^3 configuration → N of group 15
(B) ⟶ p^4 configuration → O of group 16

Stability order : $\underset{\text{Half-filled}}{p^3} > \underset{\text{Partially filled}}{p^4} >> p^1$

We know, ionisation enthalpy ($\Delta_i H$) ∝ stability of the subshell concerned.

Therefore, half-filled subshell is more stable than partially filled.

∴ $\Delta_i H$ order is $c > b >> d$

(A) is a *s*-block element (group 2) of 2nd period with s^2-configuration → Be of group 2 [fully-filled; stable]

So, the correct order of IE, or $\Delta_i H_1$ (in kJ mol^{-1}) of the 2nd period elements will be

$$\underset{(d)}{B} < \underset{(a)}{Be} \ll \underset{(b)}{O} < \underset{(c)}{N}$$
$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$
$$\underset{[801]}{(i)} \quad \underset{[899]}{(ii)} \quad \underset{[1319]}{(iii)} \quad \underset{[1902]}{(iv)}$$

The correct matching is (A)-(ii), (B)-(iii), (C)-(iv), (D)-(i)

Note The order of IE, or $\Delta_i H_1$ of 2nd period elements is

Li < B < Be < C < O < N < F < Ne

27 In general, the property (magnitudes only) that shows an opposite trend in comparison to other properties across a period is **[2020, 2 Sep Shift-I]**

(a) electronegativity
(b) electron gain enthalpy
(c) ionisation enthalpy
(d) atomic radius

Ans. ***(d)***

With increase in atomic number (*Z*) along a period, effective nuclear charge (*Z**) of the elements also increases. We know,

Z ∝ Electronegativity (χ)
∝ Electron gain enthalpy or $|\Delta_{eg} H|$
∝ Ionisation enthalpy

or $$\Delta_i H \propto \frac{1}{\text{Atomic radius } (r)}$$

So, with increase in atomic number across a period. Electronegativity, electron gain enthalpy and ionisation enthalpy increases whereas atomic radius decreases.

Note $Z^* = Z - \sigma$

Where, σ = shielding constant which can be calculated using SLATER's rule.

28 Three elements *X*, *Y* and *Z* are in the 3rd period of the periodic table. The oxides of *X*, *Y* and *Z*, respectively, are basic, amphoteric and acidic. The correct order of the atomic number of *X*, *Y* and *Z* is **[2020, 2 Sep Shift-II]**

(a) *Z* < *Y* < *X* (b) *X* < *Y* < *Z*
(c) *X* < *Z* < *Y* (d) *Y* < *X* < *Z*

Ans. ***(b)***

While moving across a period, metallic property of elements changes first into metalloids than into non-metallic nature therefore.

⇒ Metal gives basic oxides.
Metalloid produces amphoteric oxides.
Non-metal gives acidic oxides.
So, *X* → metal, *Y* → metalloid and *Z* → non-metal

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⇒ Order of atomic number : $X < Y < Z$
⇒ As, X, Y and Z belongs to 3rd period,
X can be Na or Mg
Y can be Al or Si
Z can be P or S or Cl

29 The ionic radii of O^{2-}, F^-, Na^+ and Mg^{2+} are in the order **[2020, 4 Sep Shift-I]**

(a) $O^{2-} > F^- > Mg^{2+} > Na^+$
(b) $Mg^{2+} > Na^+ > F^- > O^{2-}$
(c) $O^{2-} > F^- > Na^+ > Mg^{2+}$
(d) $F^- > O^{2-} > Na^+ > Mg^{2+}$

Ans. ***(c)***

O^{2-}, F^-, Na^+ and Mg^{2+} are isoelectronic species.

Ionic	O^{2-}	F^-	Na^+	Mg^{2+}
Number of e^-	10	10	10	10

For isoelectrons species,

$$\text{Radius} \propto \frac{-\text{ve charge}}{+\text{ ve charge}}$$

So, correct order of ionic radius is

$$O^{2-} > F^- > Na^+ > Mg^{2+}.$$

30 The correct order of the ionic radii of O^{2-}, N^{3-}, F^-, Mg^{2+}, Na^+ and Al^{3+} is **[2020, 5 Sep Shift-II]**

(a) $N^{3-} < O^{2-} < F^- < Na^+ < Mg^{2+} < Al^{3+}$
(b) $Al^{3+} < Na^+ < Mg^{2+} < O^{2-} < F^- < N^{3-}$
(c) $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$
(d) $N^{3-} < F^- < O^{2-} < Mg^{2+} < Na^+ < Al^{3+}$

Ans. ***(c)***

$$\text{Size of species} \propto \frac{1}{\text{Nuclear charge}}$$

Iso-electronic species are those atoms or ions which has the same number of electrons.

Size of species decreases with increasing protons.

More is effective nuclear charge (Z_{eff}) lesser will be ionic size.

Correct order of ionic radii

$$Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$$

31 The electron gain enthalpy (in kJ/mol) of fluorine, chlorine, bromine and iodine, respectively, are **[2020, 7 Jan Shift-I]**

(a) –333, –325, –349 and –296
(b) –296, –325, –333 and –349
(c) –333, –349, –325 and –296
(d) –349, –333, –325 and –296

Ans. ***(c)***

Electron gain enthalpy ($\Delta_{eg}H$) is the enthalpy change for converting 1 mol of isolated atoms to anions by adding electrons. All halogens have negative $\Delta_{eg}H$ (exothermic) values. Generally, $\Delta_{eg}H$ becomes less negative when comparing elements of the same group from top to bottom.

But among fluorine and chlorine there is an anomaly because inter-electron repulsion is stronger in fluorine due to its extra small size.

$\therefore \Delta_{eg}H$ is less exothermic than expected for F-atom.

Thus, the correct values of electron gain enthalpies

$$\underset{(-333)}{F} < \underset{(-349)}{Cl} > \underset{(-325)}{Br} > \underset{(-296)}{I}$$

kJ mol^{-1}

32 Within each pair of elements F and Cl, S and Se, and Li and Na, respectively, the elements that release more energy upon an electron gain are **[2020, 7 Jan Shift-II]**

(a) F, Se and Na (b) F, S and Li
(c) Cl, S and Li (d) Cl, Se and Na

Ans. ***(c)***

The first electron gain enthalpy is exothermic (or negative).

Generally, electron gain enthalpy becomes less exothermic (or less negative) when comparing elements of a group from top to bottom.

Therefore, electron gain enthalpy of S > Se and Li > Na.

But there are some exceptions to this.

One of them is the case of a group 17 elements where electron gain is most negative for Cl instead of F, due to extra small size of fluorine.

∴ Upon an electron gain, energy releases in the order :

Cl > F, S > Se and Li > Na

33 The first ionisation energy (in kJ/mol) of Na, Mg, Al and Si respectively, are : **[2020, 8 Jan Shift-I]**

(a) 496, 577, 737, 786
(b) 786, 737, 577, 496
(c) 496, 577, 786, 737
(d) 496, 737, 577, 786

Ans. ***(d)***

The first ionisation energy (in kJ/mol) of Na, Mg, Al and Si respectively are

496, 737, 577, 786

All four elements belong to the same period (3rd period) and the general trend in a period from left to right is increase in first ionisation energy, because of increase in nuclear charge and decrease in radii.

Therefore, the expected order of first ionisation enthalpies of given elements should be

Na < Mg < Al < Si

But first ionisation energies of Mg and Al show anomalous order because Mg has stable $[Ne]3s^2$ configuration and, therefore higher ionisation energy than expected, whereas Al has $[Ne]3s^2 3p^1$ configuration, which on ionisation becomes stable $[Ne]3s^2$.

∴ Its ionisation energy is less than expected.

34 The third ionisation enthalpy is minimum for : **[2020, 8 Jan Shift-I]**

(a) Mn (b) Ni
(c) Co (d) Fe

Ans. ***(d)***

Fe has minimum value of third ionisation enthalpy. Ground state electronic configuration of Fe is $[Ar]3d^6 4s^2$.

Fe^{2+} has $[Ar]3d^6$ configuration, whereas Fe^{3+} has $[Ar]3d^5$.

The latter is a stable configuration and easier to ionise Fe^{2+} to Fe^{3+} than expected.

Hence possess least value.

Ni has highest value of third ionisation enthalpy due to its greater nuclear charge and smaller size.

Due to the same reason, Co > Fe > Mn should be the order for the remaining elements, but the anomalous order is due to greater stability of Mn^{2+} having $[Ar]3d^5$ configuration than Mn^{3+} with $[Ar]3d^4$.

Whereas for Co^+, the electronic configuration is $[Ar]\,3d^7$, Thus, ionisation enthalpy needed to remove third electron is less as compared to that of Mn^{2+}.

35 The increasing order of the atomic radii of the following elements is

(A) C (B) O (C) F
(D) Cl (E) Br **[2020, 8 Jan Shift-II]**

(a) (A) < (B) < (C) < (D) < (E)
(b) (C) < (B) < (A) < (D) < (E)
(c) (D) < (C) < (B) < (A) < (E)
(d) (B) < (C) < (D) < (A) < (E)

Ans. ***(b)***

Atomic radius generally decreases as we compare elements in a period from left to right,

∴ C > O > F

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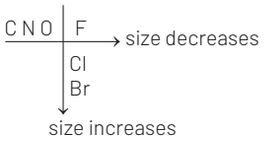
but elements present in next period are larger in size,

$\therefore$ Br > Cl > C > O > F ;



So, the correct increasing order of the atomic radii

$C < B < A < D < E$

36 B has a smaller first ionisation enthalpy than Be. Consider the following statements :

(I) It is easier to remove 2*p* electron than 2*s* electron

(II) 2*p* electron of B is more shielded from the nucleus by the inner core of electrons than the 2*s* electrons of Be

(III) 2*s* electron has more penetration power than 2*p* electron

(IV) atomic radius of B is more than Be

(atomic number B = 5, Be = 4)

The correct statements are **[2020, 9 Jan Shift-II]**

(a) (I), (II) and (III)
(b) (II), (III) and (IV)
(c) (I), (III) and (IV)
(d) (I), (II) and (IV)

Ans. ***(a)***

Statements I, II and III are correct, whereas statement IV is incorrect. It's correct form is that, atomic radius of B is less than Be.

37 The first and second ionisation enthalpies of a metal are 496 and 4560 kJ mol^{-1}, respectively. How many moles of HCl and H_2SO_4, respectively, will be needed to react completely with 1 mole of the metal hydroxide? **[2020, 9 Jan Shift-II]**

(a) 1 and 2 (b) 1 and 1
(c) 2 and 0.5 (d) 1 and 0.5

Ans. ***(d)***

A small first ionisation enthalpy (496 kJ mol^{-1}) and a great difference between first and second ionisation enthalpies (4064 kJ mol^{-1}) characterise an alkali metal (group-1) element.

It's hydroxide is a monoacidic base (*M*OH).

$\therefore$ For 1 mol of that base, 1 mol of HCl (a monoacidic acid) and 0.5 mol of H_2SO_4 (a dibasic acid) will be needed for complete reaction.

38 The process that is not endothermic in nature is **[2020, 4 Sep Shift-II]**

(a) $O^-(g) + e^- \longrightarrow O^{2-}(g)$
(b) $Na(g) \longrightarrow Na^+(g) + e^-$
(c) $H(g) + e^- \longrightarrow H^-(g)$
(d) $Ar(g) + e^- \longrightarrow Ar^-(g)$

Ans. ***(c)***

(a) $O^-(g) + e^- \longrightarrow O^{2-}(g)$ (endothermic)
(b) $Na(g) \longrightarrow Na^+(g) + e^-$ (endothermic)
(c) $H(g) + e^- \longrightarrow H^-(g)$ (exothermic)
(d) $Ar(g) + e^- \longrightarrow Ar^-(g)$ (endothermic)

Reaction (c) is not endothermic. It is exotherrnic. Electron gain ethalpy of H(*g*) is negative, due to '*s* ' configuration while that of Ar(*g*) is positive due to ns^2np^6 configuration.

Second election gain enthalpy is always positive for an atom.

Ionisation potential of an atom is positive.

39 The element having greatest difference between its first and second ionisation energy, is **[2019, 9 April Shift-I]**

(a) Ca (b) Sc
(c) Ba (d) K

Ans. ***(d)***

The electronic configuration of given elements are as follows :

$K(19) = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^1$

$Mg(12) = 1s^2\ 2s^2\ 2p^6\ 3s^2$

$Sr(38) = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$

$Sc(21) = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^2\ 3d^1$

First ionisation enthalpy (I.E.) of K is lowest among the given options. Here, the energy required to remove an electron from $4s^1$ is least as only one electron is present in the outermost shell. I.E. (I) is comparatively high for Mg and Sr and two electrons (fully-filled) are placed in *s*-orbital.

Second ionisation enthalpy of K is highest among the given options.

Now, removal of an electron occur from p^6 (fully-filled). So, high energy is required to remove the electron. From the above discussion, it can be concluded that ($I.E._2 - I.E._1$) value is maximum for K (potassium).

40 In comparison to boron, beryllium has **[2019, 12 April Shift-II]**

(a) lesser nuclear charge and lesser first ionisation enthalpy
(b) greater nuclear charge and lesser first ionisation enthalpy
(c) greater nuclear charge and greater first ionisation enthalpy
(d) lesser nuclear charge and greater first ionisation enthalpy

Ans. ***(d)***

In comparison to boron, beryllium has lesser nuclear charge and greater first ionisation enthalpy.

Electronic configuration of Be(4) = $1s^2, 2s^2$.

It possess completely filled *s*-orbitals. Hence, high amount of energy is required to pull the electron from the gaseous atom. Beryllium (4) lies left to the boron (5) and on moving from left to right an electron is added due to which nuclear charge increases from Be to B.

41 In general, the properties that decrease and increase down a group in the periodic table, respectively are **[2019, 9 Jan Shift-I]**

(a) electronegativity and atomic radius
(b) electronegativity and electron gain enthalpy
(c) electron gain enthalpy and electronegativity
(d) atomic radius and electronegativity

Ans. ***(a)***

The summary of variation of periodic properties is given in table below:

S. No.	Periodic property	Variation	
		Along a period	Along a group
1.	Atomic radius	Decreases	Increases
2.	Electron gain enthalpy	Increases	Decreases
3.	Electronegativity	Increases	Decreases

Thus, electronegativity decreases and atomic radius increases down a group in the periodic table.

42 The correct option with respect to the Pauling electronegativity values of the elements is **[2019, 11 Jan Shift-II]**

(a) P > S (b) Si < Al
(c) Te > Se (d) Ga < Ge

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Ans. ***(d)***

The electronegativity values of given elements on the Pauling scale can be shown as follows :

Period No.	Group 13	Group 14	Group 15	Group 16
3	Al (1.5)	Si (1.8)	P (2.1)	S (2.5)
4	Ga (1.6)	Ge (1.8)		Se (2.4)
5				Te (2.01)

On moving from left to right across a period, i.e. from Ga to Se, the effective nuclear charge increases and size decreases.

As a result, the value of electronegativity increases due to increase in the attraction between the outer electrons and the nucleus. Whereas on moving down the group, (i.e. from Se to Te), the atomic size increases.

As a result, the force of attraction between the outer electron and the nucleus decreases. Hence, the electronegativity decreases.

43 Which of the following atoms has the highest first ionisation energy? **[JEE Main 2016]**

(a) Na (b) K (c) Sc (d) Rb

Ans. ***(c)***

Order of first ionisation energy is Sc > Na > K > Rb.

Due to poor shielding effect, removal of one electron from 4*s* orbital is difficult as compared to 3*s*-orbital.

44 The correct order of the atomic radii of
C, Cs, Al and S is

(a) C < S < Al < Cs
(b) C < S < Cs < Al
(c) S < C < Cs < Al
(d) S < C < Al < Cs

[2019, 11 Jan Shift-I]

Ans. ***(a)***

Element	Period No.	Group No.	
C	2nd	14	
Al	3rd	13	Along the period atomic radius decreases, so, radii : Al > S.
S	3rd	16	
Cs	6th	1	

With the addition of a new shell, period number as well as atomic radius increases. It is because of the successive addition of one extra shell of electrons. So, the order of the atomic radii of the given elements will be:
C < S < Al < Cs

45 The ionic radii (in Å) of N^{3-}, O^{2-} and F^- respectively are **[JEE Main 2015]**

(a) 1.36, 1.40 and 1.71
(b) 1.36, 1.71 and 1.40
(c) 1.71, 1.40 and 1.36
(d) 1.71, 1.36 and 1.40

Ans. ***(c)***

Number of electrons in $N^{3-} = 7 + 3 = 10$
Number of electrons in $O^{2-} = 8 + 2 = 10$
Number of electrons in $F^- = 9 + 1 = 10$
Since, all the three species have each 10 electrons hence they are isoelectronic species.

It is considered that, in case of isoelectronic species as the negative charge increases, ionic radii increases and therefore the value of ionic radii are

$N^{3-} = 1.71$
(highest among the three)
$O^{2-} = 1.40$
$F^- = 1.36$
(lowest among the three)

Time Saving Technique There is no need to mug up the radius values for different ions. This particular question can be solved through following time saving.

Trick The charges on the ions indicate the size as $N^{3-} > O^{2-} > F^-$. Thus, you have to look for the option in which the above trend is followed. Option (c) is the only one in which this trend is followed. Hence, it is the correct answer.

46 Which of the following represents the correct order of increasing first ionisation enthalpy for Ca, Ba, S, Se and Ar ? **[JEE Main 2013]**

(a) Ca < S < Ba < Se < Ar
(b) S < Se < Ca < Ba < Ar
(c) Ba < Ca < Se < S < Ar
(d) Ca < Ba < S < Se < Ar

Ans. ***(c)***

Ionisation energy increases along a period from left to right and decreases down a group. The position of given elements in the periodic table is as

2	16	18
Ca	S	Ar
Ba	Se	

Thus, the order of increasing ΔH_{IE_1} is
Ba < Ca < Se < S < Ar

47 The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be **[JEE Main 2013]**

(a) – 2.55 eV (b) – 5.1 eV
(c) –10.2 eV (d) + 2.55 eV

Ans. ***(b)***

$Na \longrightarrow Na^+ + e^-$ First IE
$Na^+ + e^- \longrightarrow Na$
Electron gain enthalpy of Na^+
Because reaction is reverse so
$\Delta H_{eg} = -5.1$ eV

48 The increasing order of the ionic radii of the given isoelectronic species is **[AIEEE 2012]**

(a) Cl^-, Ca^{2+}, K^+, S^2
(b) $S^{2-}, Cl^-, Ca^{2+}, K^+$
(c) $Ca^{2+}, K^+, Cl^-, S^{2-}$
(d) $K^+, S^{2-}, Ca^{2+}, Cl^-$

Ans. ***(c)***

For isoelectronic species, $r_n \propto \frac{1}{Z}$

Here, Z is atomic number

Species	*Z*	Electrons
Cl^-	17	18
Ca^{2+}	20	18
K^+	19	18
S^{2-}	16	18

Thus, ionic size is in order
$Ca^{2+} < K^+ < Cl^- < S^{2-}$

49 Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides? **[AIEEE 2011]**

(a) $Al_2O_3 < MgO < Na_2O < K_2O$
(b) $MgO < K_2O < Al_2O_3 < Na_2O$
(c) $Na_2O < K_2O < MgO < Al_2O_3$
(d) $K_2O < Na_2O < Al_2O_3 < MgO$

Ans. ***(a)***

In a period, the nature of oxides varies from basic to acidic while in a group, basic nature of oxides increases.

Thus

Oxides ← (Decreases) — In a period, basic nature changes to acidic nature
↓ Basic nature
Increases in a group

Group	1	2	1	3
Period 3 →	Na_2O	MgO	Al_2O_3	
			(Amphoteric oxide)	
Period 4 →	K_2O	(Strongly basic)		

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Hence, basic nature of oxides are as follows

$$Al_2O_3 < MgO < Na_2O < K_2O$$

50 The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is **[AIEEE 2011]**

(a) I > Br > Cl > F (b) F > Cl > Br > I
(c) Cl > F > Br > I (d) Br > Cl > I > F

Ans. ***(c)***

As we go down the group in periodic table, atomic size increases, force of attraction for the added electron decreases. Thus, the added electron becomes loosely bound. Hence, electron gain enthalpy decreases down a group.

$$X(g) + e^- \longrightarrow X^-(g)$$

Actual order is Cl > F > Br > I

The fact that fluorine has a less electron gain enthalpy than chlorine seems to be due to the relatively greater effectiveness of 2*p*-electron in the small F-atom to repel the additional electron entering the atom than 3p-electrons in the larger Cl-atom.

51 The correct sequence which shows decreasing order of the ionic radii of the elements is **[AIEEE 2010]**

(a) $Al^{3+} > Mg^{2+} > Na^+ > F^- > O^{2-}$
(b) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$
(c) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$
(d) $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$

Ans. ***(d)***

O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+} are isoelectronic species.

For isoelectronic species, $r \propto 1/z$

Thus, larger the atomic number (effective nuclear charge) smaller is the ionic radii.

52 The set representing the correct order of ionic radius is **[AIEEE 2009]**

(a) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$
(b) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$
(c) $Li^{2+} > Na^+ > Mg^{2+} > Be^{2+}$
(d) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$

Ans. ***(b)***

The ionic radius in general increases moving top to bottom and further decreases moving left to right. So the correct order is

$$\underset{0.98\,Å}{Na^+} > \underset{0.68\,Å}{Li^+} > \underset{0.65\,Å}{Mg^{2+}} > Be^{2+}$$

53 The ionic mobility of alkali metal ions in aqueous soluton is maximum for **[AIEEE 2006]**

(a) K^+ (b) Rb^+
(c) Li^+ (d) Na^+

Ans. ***(b)***

Li^+ is having largest hydrated ionic size while Rb^+ is having smallest.

Smaller the size, greater is the mobility.

54 The increasing order of the first ionisation enthalpies of the elements B, P, S and F (lowest first) is **[AIEEE 2006]**

(a) F < S < P < B
(b) P < S < B < F
(c) B < P < S < F
(d) B < S < P < F

Ans. ***(d)***

Examine the positions in periodic table.

Group	13	14	15	16	17
	B	C	N	O	F
			P	S	

Ionisation enthalpy increases along a period due to increased nuclear charge and decreased atomic radii. While in a group, it decreases from top to bottom. Along with this trend ionisation enthalpy is highest for the elements possessing half filled and sable electronic configuration.

Since, phosphorus is having stable half-filled configuration. Hence, order is B < S < P < F.

55 Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements give the correct picture? **[AIEEE 2006]**

(a) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group
(b) In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group
(c) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens
(d) In alkali metals, the reactivity increases but in the halogens it decreases with increase in atomic number down the group

Ans. ***(d)***

The chemical reactivity of alkali metals is due to their ability to loose electron more readily than other elements. Since, the tendency to loose electron by alkali metals increases down the group, therefore, their chemical reactivity increases down the group.

On the other hand, chemical reactivity of halogens is due to their ability to gain extra electron more readily than other elements. Since the tendency to gain electron by halogens decreases down the group, hence their chemical reactivity decreases down the group.

56 In which of the following arrangements the order is not according to the property indicated against it ? **[AIEEE 2005]**

(a) Li < Na < K < Rb Increasing metallic radius
(b) I < Br < F < Cl Increasing electron gain enthalpy (with negative sign)
(c) B < C < N < O Increasing first ionisation enthalpy
(d) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ Increasing ionic size

Ans. ***(c)***

(a) Metallic radii increase in a group from top to bottom.
Thus, Li < Na < K < Rb—True

(b) Electron gain enthalpy of Cl > F and decreases along a group.
Thus, I < Br < F < Cl is true.

(c) Ionisation enthalpy increases along a period from left to right but due to presence of half filled orbitals in N, ionisation enthalpy of N > O.
Thus, B < C < N < O is incorrect.

(d) Higher the negative charges, larger is their ionic radii
$Al^{+}_{3} < Mg^{2+} < Na^+ < F^-$ is also true.

57 Based on lattice energy and other considerations which one of the following alkali metal chlorides is expected to have the highest melting point ? **[AIEEE 2005]**

(a) RbCl (b) KCl (c) NaCl (d) LiCl

Ans. ***(c)***

As we go down in the group, ionic character increases, hence melting point of halides should increase but NaCl has the highest melting point (800°C) due to its high lattice energy.

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58 Which one of the following ions has the highest value of ionic radius ? **[AIEEE 2004]**

(a) Li^+ (b) B^{3+} (c) O^{2-} (d) F^-

Ans. ***(c)***

All the ions belong to same period, thus for them cations will be smaller than anions. Now, O^{2-} and F^- are isoelectronic and $r_n \propto \frac{1}{Z}$

Thus, ionic radius of

$O^{2-}(Z=8) > F^-(Z=9)$

59 The formation of the oxide ion $O^{2-}(g)$ requires first an exothermic and then an endothermic step as shown below

$$O(g) + e^- = O^-(g); \quad \Delta H° = -142\,kJ\,mol^{-1}$$

$$O^-(g) + e^- = O^{2-}(g); \quad \Delta H° = 844\,kJ\,mol^{-1}$$

This is because **[AIEEE 2004]**

(a) oxygen is more electronegative
(b) oxygen has high electron affinity
(c) O^- ion will tend to resist the addition of another electron
(d) O^- ion has comparatively larger size than oxygen atom

Ans. ***(c)***

$$O^-(g) + e^- \longrightarrow O^{2-}(g); \quad \Delta H° = 844\,kJ\,mol^{-1}$$

This process is unfavourable in the gas phase because the resulting increase in electron-electron repulsion overweighs the stability gained by achieving the noble gas configuration.

60 Which among the following factors is the most important in making fluorine the strongest oxidising agent ? **[AIEEE 2004]**

(a) Electron affinity
(b) Ionisation enthalpy
(c) Hydration enthalpy
(d) Bond dissociation energy

Ans. ***(c)***

F_2 has the most negative $\Delta G°$ value which is dependent on hydration enthalpy.

61 Among Al_2O_3, SiO_2, P_2O_3 and SO_2 the correct order of acid strength is **[AIEEE 2004]**

(a) $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$
(b) $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$
(c) $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$
(d) $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$

Ans. ***(d)***

While moving along a group from top to bottom, acidic nature of oxides decreases and along a period from left to right, acidic nature increases.

	Al	Si	P	S
Z	13	14	15	16
	Al_2O_3	SiO_2	P_2O_3	SO_2

amphoteric → acidic → max. acidic

Thus, $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$

62 The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are, respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy? **[AIEEE 2003]**

(a) V
(b) Cr
(c) Mn
(d) Fe

Ans. ***(b)***

$Fe^+(26) = [Ar]\,3d^6, 4s^1$
$Mn^+(25) = [Ar]\,3d^5, 4s^1$
$V^+(23) = [Ar]3d^2, 4s^2$
$Cr^+(24) = [Ar]3d^5, 4s^0$ [By first IP]

The electronic configuration of Cr^+ is most stable, hence formation of Cr^{2+} by second IP requires maximum enthalpy.

63 Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} have ionic radii in the increasing order as **[AIEEE 2002]**

(a) $La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+}$
(b) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
(c) $La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+}$
(d) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$

Ans. ***(b)***

$$r_n\,(\text{radius}) \propto \frac{1}{Z}$$

Thus, $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$.

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14

General Principles and Processes of Isolation of Metals

TOPIC 1

Occurrence, Thermodynamic and Electrochemical Principles of Metallurgy

01 Calamine and malachite, respectively, are the ores of

[2021, 1 Sep Shift-II]

(a) nickel and aluminium
(b) zinc and copper
(c) copper and iron
(d) aluminium and zinc

Ans. ***(b)***

Calamine is the ore of Zn and is found as zinc carbonate ($ZnCO_3$), where malachite is the ore of copper and is found as copper hydroxide [$Cu(OH)_2$] and copper carbonate [$CuCO_3$].

02 Match List-I with List-II.

	List-I (Name of ore/mineral)		**List-I** (Chemical formula)
A.	Calamine	1.	ZnS
B.	Malachite	2.	$FeCO_3$
C.	Siderite	3.	$ZnCO_3$
D.	Sphalerite	4.	$CuCO_3 \cdot Cu(OH)_2$

Choose the most appropriate answer from the options given below

[2021, 27 Aug Shift-II]

	A	B	C	D		A	B	C	D
(a)	3	4	2	1	(b)	3	4	1	2
(c)	4	3	1	2	(d)	3	2	4	1

Ans. ***(a)***

Ore and their chemical formula are given below

(A) Calamine (3) $ZnCO_3$
(B) Malachite (4) $CuCO_3 \cdot Cu(OH)_2$
(C) Siderite (2) $FeCO_3$
(D) Sphalerite (1) ZnS

Therefore, the correct match is A → 3, B → 4, C → 2, D → 1.

03 The statement that is incorrect about Ellingham diagram is

[2021, 27 July Shift-I]

(a) provides idea about the reaction rate.
(b) provides idea about free energy change.
(c) provides idea about changes in the phases during the reaction.
(d) provides idea about reduction of metal oxide.

Ans. ***(a)***

Ellingham diagram is a plot between $\Delta G°$ and temperature (T). It compares thermal stability of metal oxide as well as reducing power of metals.

It does not give any information regarding rate of reaction.

04 Given below are two statements.

Statement I The choice of reducing agent for metals extraction can be made by using Ellingham diagram, a plot of ΔG *vs* temperature.

Statement II The value of ΔS increases from left to right in Ellingham diagram.

In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 26 Aug Shift-I]

(a) Both statement I and statement II are true.
(b) Statement I is false but statement II is true.
(c) Both statement I and statement II are false.
(d) Statement I is true but statement II is false.

Ans. ***(d)***

The Ellingham diagram, a plot of ΔG *vs* temperature is used to choose reducing agents for metal extraction. Any element will reduce the oxide of other metal if it lie above that element in Ellingham diagram because the free energy change will become more negative. Hence, statement I is true.

In Ellingham diagram the value of entropy change (ΔS) decreases from left to right.

Hence, statement II is false.

05 Sulphide ion is soft base and its ores are common for metals

(A) Pb (B) Al (C) Ag (D) Mg

Choose the correct answer from the options given below

[2021, 22 July Shift-II]

(a) (A) and (C) only
(b) (A) and (D) only
(c) (A) and (B) only
(d) (C) and (D) only

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Ans. *(a)*

Pb and Ag are found as sulphide ore as these ores are frequently associated with a range of important metals, most commonly copper, lead, nickel, zinc, silver, and gold.

Metal	Common ore
Pb	PbS (Galena)
Al	$Al_2O_3 \cdot 2H_2O$ (Bauxite)
Ag	Ag_2S (Argentite)
Mg	$KCl \cdot MgCl_2 \cdot 6H_2O$ (Carnallite)

06 Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Sharp glass edge becomes smooth on heating it upto its melting point.

Reason (R) The viscosity of glass decreases on melting.

Choose the most appropriate answer from the options given below. **[2021, 20 July Shift-I]**

(a) A is true but R is false

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is false but R is true.

(d) Both A and R are true and R is the correct explanation of A.

Ans. *(b)*

On heating the glass, it melts and takes up rounded shape at the edges, which has minimum surface area. This is due to the property of surface tension of liquids and not due to decrease in viscosity.

Viscosity generally decreases as the temperature increases.

Hence, both A and R are true but R is not the correct explanation of A.

07 Match List-I and List-II.

List-I	List-II
A. Haematite	1. $Al_2O_3 \cdot x\,H_2O$
B. Bauxite	2. Fe_2O_3
C. Magnetite	3. $CuCO_3 \cdot Cu(OH)_2$
D. Malachite	4. Fe_3O_4

Choose the correct answer from the options given below. **[2021, 17 March Shift-II]**

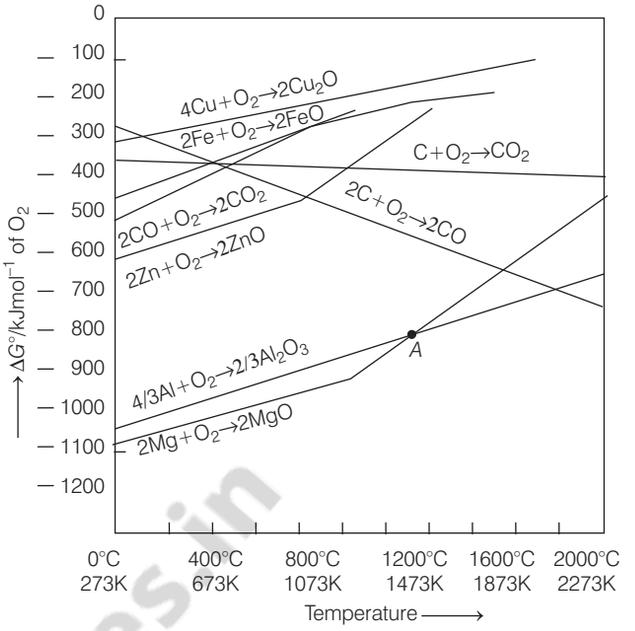
	A	B	C	D		A	B	C	D
(a)	2	3	1	4	(b)	4	1	2	3
(c)	1	3	2	4	(d)	2	1	4	3

Ans. *(d)*

Correct matches are A-2, B-1, C-4, D-3.

Ore	Formula
Haematite	Fe_2O_3
Bauxite	$Al_2O_3 \cdot xH_2O$
Magnetite	Fe_3O_4
Malachite	$CuCO_3 \cdot Cu(OH)_2$

08 The point of intersection and sudden increase in the slope, in the diagram given below, respectively, indicates.



[2021, 17 March Shift-I]

(a) $\Delta G = 0$ and melting or boiling point of the metal oxide

(b) $\Delta G > 0$ and decomposition of the metal oxide

(c) $\Delta G < 0$ and decomposition of the metal oxide

(d) $\Delta G = 0$ and reduction of the metal oxide

Ans. *(a)*

At intersection point $\Delta G = 0$, which represents the equilibrium point and sudden increase in slope is due to melting or boiling point of the metal oxide.

According to Gibb's free rule,

$$\Delta G = \Delta H - T\Delta S$$

where, ΔH = change in enthalpy

ΔG = change in Gibb's free energy

ΔS = change in entropy

We can see that ΔG is dependent on ΔS.

So, when the phase changes ($s \rightarrow l$ or $l \rightarrow g$) the entropy increases and hence, slope increases.

09 Match List-I with List-II.

List-I	List-II
A. Siderite	(i) Cu
B. Calamine	(ii) Ca
C. Malachite	(iii) Fe
D. Cryolite	(iv) Al
	(v) Zn

Chose the correct answer from the options given below. **[2021, 26 Feb Shift-II]**

	A	B	C	D		A	B	C	D
(a)	(iii)	(i)	(v)	(ii)	(b)	(i)	(ii)	(v)	(iii)
(c)	(iii)	(v)	(i)	(iv)	(d)	(i)	(ii)	(iii)	(iv)

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Ans. ***(c)***

(A) Siderite ($FeCO_3$) is the ore of Fe $\Rightarrow$(iii) of List-II.

(B) Calamine ($ZnCO_3$) is the ore of Zn $\Rightarrow$(v) of List - II.

(C) Malachite [$CuCO_3 \cdot Cu(OH)_2$] is the ore of Cu $\Rightarrow$(i) of List II.

(D) Cryolite (Na_3AlF_6) is the ore of Al $\Rightarrow$(iv) of List II. (as well as F_2)

So, option -(c) is the correct matching.

Note Siderite and calamine are carbonate ores whereas malachite is basic carbonate ore. Cryolite is the thioxide ore.

10 Match List-I with List-II.

	List-I (Ore)		List-II (Element present)
A.	Kernite	(i)	Tin
B.	Cassiterite	(ii)	Boron
C.	Calamine	(iii)	Fluorine
D.	Cryolite	(iv)	Zinc

Choose the most appropriate answer from the options given below. **[2021, 26 Feb Shift-I]**

	A	B	C	D		A	B	C	D
(a)	(i)	(iii)	(iv)	(ii)	(b)	(ii)	(i)	(iv)	(iii)
(c)	(ii)	(iv)	(i)	(iii)	(d)	(iii)	(i)	(ii)	(iv)

Ans. ***(b)***

(A) Kernite ($Na_2B_4O_7 \cdot 4H_2O$) is sodium tetraborate tetrahydrate. It is also called rasovite. Kernite is also written as $Na_2B_4O_6(OH)_2 \cdot 3H_2O$
It is an ore of boron (ii).

(B) Cassiterite (SnO_2) is the oxide.
It is an ore of tin (i).

(C) Calamine ($ZnCO_3$) is zinc carbonate. It is also called smith sonite.
It is an ore of zinc (iv).

(D) Cryolite (Na_3AlF_6) is sodium hexafluoroaluminate.
It is an ore of fluorine (iii).
So, correct match is (A)-(ii), (B)-(i), (C)-(iv), (D)-(iii).

11 Ellingham diagram is a graphical representation of **[2021, 25 Feb Shift-I]**

(a) ΔG *vs* T (b) ΔH *vs* T
(c) ΔG *vs* p (d) $(\Delta G - T\Delta S)$ *vs* T

Ans. ***(a)***

Ellingham diagram is the graphical representation of ΔG *vs* T. For the formation of oxides of elements similar diagrams can also be constructed for sulphides and halides. Such diagrams can help us in pridicting the feasibility of thermal reduction of an ore.

12 Match List-I with List-II.

	List I (Metal)		List II (Ores)
A.	Aluminium	1.	Siderite
B.	Iron	2.	Calamine
C.	Copper	3.	Kaolinite
D.	Zinc	4.	Malachite

Choose the correct answer from the options given below. **[2021, 24 Feb Shift-II]**

	A	B	C	D
(a)	4	3	2	1
(b)	2	4	1	3
(c)	1	2	3	4
(d)	3	1	4	2

Ans. ***(d)***

(A) Siderite $\rightarrow FeCO_3$
Siderite is a mineral composed of iron (II) carbonate ($FeCO_3$).

(B) Calamine $\rightarrow ZnCO_3$
Calamine is used to treat mild itchiness and contain zinc in its formula.

(C) Kaolinite $\rightarrow Al_2(OH)_4 \cdot Si_2O_5$
Kaolinite is a type of clay found in nature. It is a dioctahedral pyrosilicate clay containing Si_2O_5.

(D) Malachite $\rightarrow Cu(OH)_2 \cdot CuCO_3$
Malachite is a copper carbonate hydroxide mineral, with the formula $Cu_2CO_3(OH)_2$.

13 An Ellingham diagram provides information about **[2020, 5 Sep Shift-I]**

(a) the kinetics of the reduction process.
(b) the pressure dependence of the standard electrode potentials of reduction reactions involved in the extraction of metals.
(c) the temperature dependence of the standard Gibbs energies of formation of some metal oxides.
(d) the conditions of pH and potential under which a species is thermodynamically stable.

Ans. ***(c)***

Ellingham diagram provides information about temperature dependence of the standard Gibbs energies of formation of some metal oxides.

It predicts the feasibility of thermal reduction of the ore. The criterion of feasibility is that at given temperature, Gibbs energy of the reaction must be negative.

14 For a reaction,

$$4M(s) + nO_2(g) \longrightarrow 2M_2O_n(s)$$

The free energy change is plotted as a function of temperature. The temperature below which the oxide is stable could be inferred from the plot as the point at which **[2020, 6 Sep Shift-II]**

(a) the slope changes from negative to positive
(b) the free energy change shows a change from negative to positive value
(c) the slope changes from positive to negative
(d) the slope changes from positive to zero

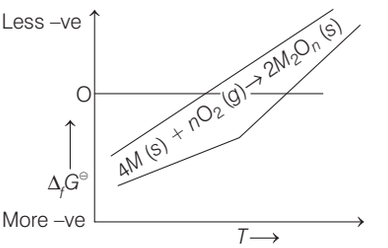
Ans. ***(b)***

Ellingham diagram usually consists of plots of $\Delta_f G^\ominus$ *vs* T for the formation of oxide of various elements.

For the reaction,

$$4M(s) + nO_2(g) \longrightarrow 2M_2O_n(s)$$

free energy change plot as a function of temperature is as follows :



In this reaction, O_2 (a gas) is used up and $M_2O_n(s)$, a solid is formed. Since, gases have higher entropy than solids, ΔS becomes negative. Thus, on increasing the temperature, $T\Delta_f S^\ominus$ becomes more negative, hence $\Delta_f G^\ominus$ becomes less negative which is shown in figure.

The slope of the curves for the formation of metal oxides is positive as $\Delta_f G^\ominus$ becomes less negative.

Any metal oxide having lower value of $\Delta_f G^\ominus$ is more stable as compared to metal oxide with higher value of $\Delta_f G^\ominus$.

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From the graph it is evident, that the temperature below which the oxide is stable, is the point at which free energy change shows a change from negative to positive.

15 The incorrect statement is **[2020, 6 Sep Shift-I]**

(a) bronze is an alloy of copper and tin.
(b) cast iron is used to manufacture wrought iron.
(c) german silver is an alloy of zinc, copper and nickel.
(d) brass is an alloy of copper and nickel.

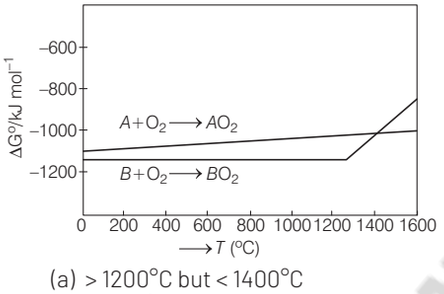
Ans. ***(d)***

Statements (d) is incorrect whereas all other statements are correct.

(a) Bronze is an alloy of Cu (96%) and Sn (4%).
(b) Cast iron is used to manufacture wrought iron.
(c) German silver is an alloy of 50% Cu, 30% Zn and 20% Ni.
(d) Brass is an alloy of 70% Cu and 30% Zn.

Hence, the incorrect option is (d).

16 According to the following diagram, *A* reduces BO_2 when the temperature is **[2020, 9 Jan Shift-I]**



(a) > 1200°C but < 1400°C
(b) >1400° C
(c) <1200°C
(d) <1400°C

Ans. ***(b)***

A metal with more negative value of $\Delta G°$ of oxide formation reduces oxide of another metal which has less negative value of $\Delta G°$. Value of $\Delta G°$ of oxide formation plotted against temperature (as given in question) is called Ellingham's diagram.

From the graph given, $\Delta G°$ of BO_2 formation is more negative than AO_2 upto 1400°C.

$\therefore$ *B* can reduce AO_2 at these conditions. But above 1400°C, AO_2 formation has more negative $\Delta G°$ than BO_2,

$\therefore$ *A* can reduce BO_2.

17 With respect to an ore, Ellingham diagram helps to predict the feasibility of its **[2019, 9 April Shift-I]**

(a) electrolysis
(b) zone refining
(c) vapour phase refining
(d) thermal reduction

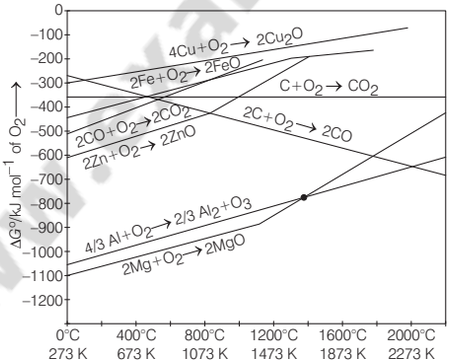
Ans. ***(d)***

With respect to an ore, Ellingham diagram helps to predict the feasibility of its thermal reduction. It is a graph representation of Gibbs energy change *versus* absolute temperature.

Generally, the diagram consists of plots of $\Delta G°$ *versus* T for the formation of oxides of elements

$$2xM(s) + O_2(g) \longrightarrow \underset{\text{Thermal reduction product}}{2M_xO(s)}$$

In this reaction, amount of gas decreases thus, randomness decreases. Hence, ΔS becomes negative. Therefore, the value of free energy increases with increase in temperature. There is a point in a curve below which ΔG is negative. So, M_xO is stable. Above this point, M_xO will decompose on its own.



Gibbs energy ($\Delta G°$) *versus* *T* plots (schematic) for the formation of some oxides (Ellingham diagram)

18 The ore that contains the metal in the form of fluoride is **[2019, 9 April Shift-I]**

(a) magnetite
(b) sphalerite
(c) malachite
(d) cryolite

Ans. ***(d)***

Cryolite ore (Na_3AlF_6, sodium hexafluoroaluminate) contain fluorine while other given options such as malachite ($Cu_2(CO)_3(OH)_2$), sphalerite ((Zn,Fe)S) and bauxite (Al_2O_3) does not contain fluorine.

19 The one that is not a carbonate ore is **[2019, 9 April Shift-II]**

(a) siderite (b) calamine
(c) malachite (d) bauxite

Ans. ***(d)***

Bauxite is not a carbonate ore. Its chemical formula is Al_2O_3 or $AlO_x(OH)_{3-2x}$, where $0 < x < 1$. Chemical formula of other ores given in options are as follows:

Siderite-$FeCO_3$
Calamine-$ZnCO_3$
Malachite-$CuCO_3 \cdot Cu(OH)_2$

20 The alloy used in the construction of aircrafts is **[2019, 10 April Shift-II]**

(a) Mg-Zn (b) Mg-Mn
(c) Mg-Sn (d) Mg-Al

Ans. ***(d)***

Names of magnesium alloys are given by two letters followed by two numbers. The common alloying elements are *A* (Aluminium), *Z* (zinc), *T* (tin), *M* (manganese) etc. Numbers indicate respective nominal compositions of main alloying elements, e.g.

'*AZ* 91' implies the composition of the alloy as : Al = 9%, Zn = 1% and Mg = 100 – (9 + 1) = 90%

Among the alloys given, Mg – Al (Magnalium ; Mg = 5%, Al =95%) is being light, tough and strong, hence it is used in aircrafts.

21 The ore that contains both iron and copper is **[2019, 9 Jan Shift-I]**

(a) malachite
(b) azurite
(c) dolomite
(d) copper pyrites

Ans. ***(d)***

The formulae of the given ores are as follows:

Malachite	: $CuCO_3 \cdot Cu(OH)_2$
Copper pyrites	: $CuFeS_2$
Dolomite	: $CaMg(CO_3)_2$
Azurite	: $Cu_3(CO)_3(OH)_2$

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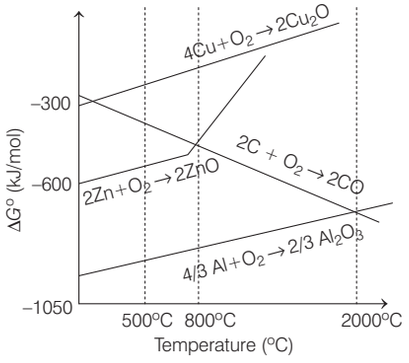
22 The correct statement regarding the given Ellingham diagram is



[2019, 10 Jan Shift-II]

(a) At 800°C, Cu can be used for the extraction of Zn from ZnO
(b) At 1400°C, Al can be used for the extraction of Zn from ZnO
(c) At 500°C, coke can be used for the extraction of Zn from ZnO
(d) Coke cannot be used for the extraction of Cu from Cu_2O

Ans. ***(b)***

From the Ellingham diagram, we can say that any oxide with lower value of $\Delta G°$ is more stable than a oxide with higher value of $\Delta G°$.

We can also predict that the oxide placed higher in the diagram can be reduced by the element involved in the formation of its oxide placed lower at that temperature in the diagram. It is happening in case of ZnO for its reduction by Al at 1400°C.

23 Match the ores (Column A) with the metals (Column B).

	Column A (Ores)		Column B (Metals)
A.	Siderite	P.	Zinc
B.	Kaolinite	Q.	Copper
C.	Malachite	R.	Iron
D.	Calamine	S.	Aluminium

(a) A - P; B- Q; C - R; D- S
(b) A - R; B- S; C - P; D- Q
(c) A - Q; B- R; C - S; D- P
(d) A - R; B- S; C - Q; D- P

[2019, 11 Jan Shift-I]

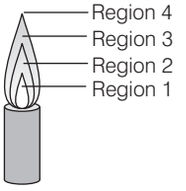
Ans. ***(d)***

The correct match is: A → R; B → S; C → Q; D → P.

(A) Siderite is an ore of iron with molecular formula $FeCO_3(R)$.
(B) Kaolinite is an ore of aluminium with molecular formula $Al_2Si_2(OH)_2O_5$ (S).
(C) Malachite is an ore of copper with molecular formula $CuCO_3 \cdot Cu(OH)_2$ (Q).
(D) Calamine is an ore of zinc with molecular formula $ZnCO_3$(P).

24 The hottest region of Bunsen flame shown in the figure given below is

[JEE Main 2016]



(a) region 2 (b) region 3
(c) region 4 (d) region 1

Ans. ***(a)***

Region 1 (Pre-heating zone)
Region 2 (Primary combustion zone, hottest zone)
Region 3 (Internal zone)
Region 4 (Secondary reaction zone)

25 Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?

[AIEEE 2008]

(a) Metal sulphides are thermodynamically more stable than CS_2
(b) CO_2 is thermodynamically more stable than CS_2
(c) Metal sulphides are less stable than the corresponding oxides
(d) CO_2 is more volatile than CS_2

Ans. ***(c)***

$2MS + C \longrightarrow 2M + CS_2$; $\Delta G_1 = +ve$
$2MO + C \longrightarrow 2M + CO_2$; $\Delta G_2 = -ve$

The value of ΔG for the formation of CO_2 is negative, *i.e.*, it is thermodynamically more stable than CS_2. Also, metal sulphides are thermodynamically more stable than CS_2.

Metal sulphides are more stable than the corresponding oxides, so they are roasted to convert into less stable oxides.

26 Consider the following reactions at 1100°C

(I) $2C + O_2 \rightarrow 2CO$, $\Delta G° = -460\ kJ\ mol^{-1}$
(II) $2Zn + O_2 \rightarrow 2ZnO$, $\Delta G° = -360\ kJ\ mol^{-1}$

Based on these, select correct alternative. **[AIEEE 2002]**

(a) zinc can be oxidised by CO
(b) zinc oxide can be reduced by carbon
(c) Both (a) and (b)
(d) None of the above

Ans. ***(b)***

$ZnO + C \longrightarrow Zn + CO$,
$\Delta G° = -ve$

Hence, this is spontaneous.

TOPIC 2
Extraction and Isolation of Metals

27 Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Aluminium is extracted from bauxite by the electrolysis of molten mixture of Al_2O_3 with cryolite.

Reason (R) The oxidation state of Al in cryolite is +3 .

In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 31 Aug Shift-I]

(a) (A) is true but (R) is false
(b) (A) is false but (R) is true.
(c) Both (A) and (R) are true and (R) is the correct explanation of (A).
(d) Both (A) and (R) are true but (R) is not the correct explanation of (A).

Ans. ***(d)***

Aluminium is reactive metal. So, aluminium is extracted by electrolysis of alumina with molten mixture of cryolite. Hence, Assertion is true.

Cryolite has molecular formula Na_3AlF_6.

Oxidation state of Al in Na_3AlF_6

$3 \times (+1) + Al + 6 \times (-1) = 0$
$3 + Al - 6 = 0 \Rightarrow Al = +3$

Hence, Reason is true.

Oxidation state cannot explain that Al is extracted from bauxite by electrolysis.

∴ The correct option is (d).

28 Given below are two statements.

Statement I Sphalerite is a sulphide ore of zinc and copper glance is a sulphide ore of copper.

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Statement II It is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants' in a froth flotation method.

Choose the most appropriate answer from the options given below. **[2021, 26 Aug Shift-II]**

(a) Statement I is true but statement II is false.
(b) Both statement I and statement II are true.
(c) Statement I is false but statement II is true.
(d) Both statement I and statement II are false.

Ans. ***(b)***

Both statements I and II are true.

Sphalerite –ZnS (Sulphide ore of zinc).

Copper glance – Cu_2S (Sulphide ore of copper).

It is possible to separate two sulphide ores by adjusting the proportion of oil to water or by using depressants.

29 The addition of silica during the extraction of copper from its sulphide ore **[2021, 27 July Shift-II]**

(a) converts copper sulphide into copper silicate
(b) converts iron oxide into iron silicate
(c) reduces copper sulphide into metallic copper
(d) reduces the melting point of the reaction mixture

Ans. ***(b)***

Silica is used to remove FeO impurity from the ore of copper. The impurities of iron oxide combine with silica and form insoluble slag.

$$\underset{\text{Basic impurity}}{FeO} + \underset{\text{Acidic flux}}{SiO_2} \xrightarrow{\text{Fuse}} \underset{\text{Iron silicate (slag)}}{FeSiO_3}$$

30 Match List I with List II : (Both having metallurgical terms)

	List I		List II
(A)	Concentration of Ag ore	I.	Reverberatory furnace
(B)	Blast furnace	II.	Pig iron
(C)	Blister copper	III.	Leaching with dilute NaCN solution
(D)	Froth floatation method	IV.	Sulphide ores

Choose the correct answer from the options given below. **[2021, 25 July Shift-II]**

	A	B	C	D
(a)	III	II	I	IV
(b)	III	IV	I	II
(c)	IV	I	III	II
(d)	IV	III	II	I

Ans. ***(a)***

A. Concentration of Ag ore is performed by leaching with dilute NaCN solution.
B. Pig iron is formed in blast furnace.
C. Blister copper is produced in bessemer converter.
D. Froth floatation method is used for sulphide ores. It is selectively separating hydrophobic materials from hydrophilic.

Note During extraction of Cu reverberatory furnace is involved.

31 In the leaching of alumina from bauxite, the ore expected to leach out in the process by reacting with NaOH is **[2021, 25 July Shift-I]**

(a) TiO_2 (b) Fe_2O_3
(c) ZnO (d) SiO_2

Ans. ***(d)***

In bauxite impurities of Fe_2O_3, TiO_2 and SiO_2 are present, Fe_2O_3 and TiO_2 are basic oxides, it does not reacts with or dissolve in NaOH whereas SiO_2 is acidic oxide it dissolve in NaOH, hence leach outeasily.

$$\underset{\text{Silica}}{SiO_2} + 2NaOH \rightarrow \underset{\text{Sodium hydroxide}}{Na_2SiO}(aq) + H_2O$$

32 Consider two chemical reactions (*A*) and (*B*) that take place during metallurgical process :

$$(A)\ ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

$$(B)\ 2ZnS(s) + 3O_2(g) \xrightarrow{\Delta} 2ZnO(s) + 2SO_2(g)$$

The correct option of names given to them respectively is **[2021, 20 July Shift-II]**

(a) (*A*) is calcination and (*B*) is roasting
(b) Both (*A*) and (*B*) are producing same product so both are roasting
(c) Both (*A*) and (*B*) are producing same product so both are calcination
(d) (*A*) is roasting and (*B*) is calcination

Ans. ***(a)***

(A) Heating of carbonate ores in absence or limited supply of air or oxygen is called calcination.

$$ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

(B) Roasting includes heating of sulphide ore in the presence of oxygen or air.

$$2ZnS(s) + 3O_2(g) \xrightarrow{\Delta} 2ZnO(s) + 2SO_2(g)$$

Therefore, (*A*) is calcination process while (*B*) is roasting.

33 Match List-I with List-II.

	List-I		List-II
A.	Mercury	1.	Vapour phase refining
B.	Copper	2.	Distillation refining
C.	Silicon	3.	Electrolytic refining
D.	Nickel	4.	Zone refining

Choose the most appropriate answer the option given below **[2021, 18 March Shift-II]**

	A	B	C	D		A	B	C	D
(a)	1	4	2	3	(b)	2	3	1	4
(c)	2	3	4	1	(d)	2	4	3	1

Ans. ***(c)***

(A) The pyrometallurgical extraction of mercury from its ore is essentially a distillation process.
(B) The purification of metals by electrolysis is commonly applied to copper. A large piece of impure copper is used as the anode with a thin strip of pure copper as the cathode.
(C) Zone refining is a very useful method to get metals with very high purity such as silicon and germanium. It is also referred as zone melting.
(D) Mond's process for extraction of nickel and van-Arkel method for preparing ultra-pure titanium are based on the principle of vapour phase refining.

Hence, correct match is (A-2), (B-3), (C-4), (D-1).

34 The chemical that is added to reduce the melting point of the reaction mixture during the extraction of aluminium is **[2021, 18 March Shift-I]**

(a) cryolite (b) bauxite
(c) calamine (d) kaolite

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Ans. ***(a)***

In the extraction of aluminium by electrolytic process, cryolite is added to reduce the melting point of the mixture. The use of cryolite reduces some of the energy cost involved in extracting aluminium.

Reactions involved in the electrolysis are given below

$$Al_2O_3 \rightleftharpoons 2Al^{+3} + 3O^{-2}$$
$$Na_3AlF_6 \rightleftharpoons 3Na^{+} + Al^{+3} + 6F^{-}$$
$$CaF_2 \rightleftharpoons Ca^{+2} + 2F^{-}$$

At cathode : $Al^{3+} + 3e^{-} \longrightarrow Al$ (reduction)

At anode : $C + O^{2-} \longrightarrow CO + 2e^{-}$ (oxidation)

$$C + 2O_2^{-} \longrightarrow CO_2 + 4e^{-}$$

35 Which of the following reduction reaction cannot be carried out with coke? **[2021, 16 March Shift-II]**

(a) $Al_2O_3 \longrightarrow Al$ (b) $ZnO \longrightarrow Zn$

(c) $Fe_2O_3 \longrightarrow Fe$ (d) $Cu_2O \longrightarrow Cu$

Ans. ***(a)***

Reduction of alumina (Al_2O_3) to Al cannot be achieved by carbon reduction. As aluminium has greater reactivity with oxygen than carbon and hence cannot be reduced by carbon. So, electrometallurgy (Hall-Heroult process) is used to get Al.

$$2Al_2O_3(l) + 3C \longrightarrow 4Al + 3CO_2$$

Rest oxides can be reduced by coke as follows

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
$$Cu_2O + C \longrightarrow 2Cu + CO$$
$$ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO$$

36 The process that involves the removal of sulphur from the ores is **[2021, 16 March Shift-I]**

(a) smelting (b) roasting (c) leaching (d) refining

Ans. ***(b)***

The process that involves the removal of sulphur from the ores is called roasting.

In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal.

Some of the reactions involving sulphide ores are

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$
$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

37 Which of the following ore is concentrated using group 1 cyanide salt ? **[2021, 24 Feb Shift-I]**

(a) Calamine (b) Malachite (c) Siderite (d) Sphalerite

Ans. ***(d)***

The chemical formulas of given ore in options are as follows

Sphalerite ore : ZnS ; Calamine ore : $ZnCO_3$

Siderite ore : $FeCO_3$; Malachite ore : $Cu(OH)_2 \cdot CuCO_3$

Sphalerite ore containing ZnS is concentrated using group is cyanide salt (NaCN) as a depressant by froth flotation method.

38 Cast iron is used for the manufacture of **[2020, 2 Sep Shift-II]**

(a) wrought iron and pig iron

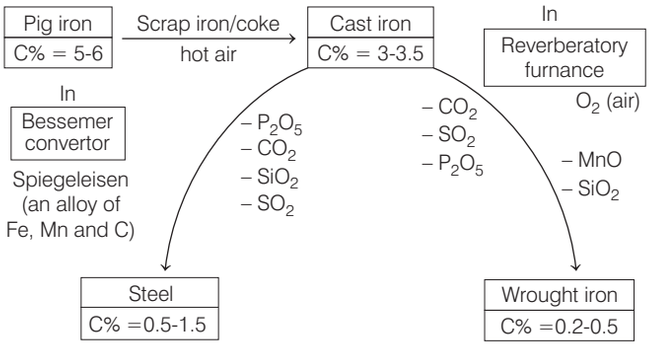
(b) pig iron, scarp iron and steel

(c) wrought iron, pig iron and steel

(d) wrought iron and steel

Ans. ***(d)***

Consider the following flow sheet :



So, it is clear from the flow chart that cast iron is used in the manufacture of wrought iron and steel.

39 Among statements (A)-(D), the correct ones are :

(A) Limestone is decomposed to CaO during the extraction of iron from its oxides.

(B) In the extraction of silver, silver is extracted as an anionic complex.

(C) Nickel is purified by Mond's process.

(D) Zr and Ti are purified by van-Arkel method. **[2020, 4 Sep Shift-I]**

(a) (A), (B), (C) and (D) (b) (A), (C) and (D) only

(c) (C) and (D) only (d) (B), (C) and (D) only

Ans. ***(a)***

Statements (A), (B), (C) and (D) are correct.

(A) $\underset{\text{Limestone}}{CaCO_3} \xrightarrow{\Delta} CaO + \underset{\text{Gas}}{CO_2}$

(B) Ag with $CN^{\ominus}$ form cyanide complex $[Ag(CN)_2]^{\ominus}$.

$$Ag + CN^{\ominus} \longrightarrow [Ag(CN)_2]^{\ominus}$$

(C) Mond's process is used to purification of Ni.

(D) van-Arkel method is used to purification of Zr and Ti.

40 The processes of calcination and roasting in metallurgical industries, respectively, can lead to **[2020, 4 Sep Shift-II]**

(a) global warming and acid rain

(b) global warming and photochemical smog

(c) photochemical smog and ozone layer depletion

(d) photochemical smog and global warming

Ans. ***(a)***

(a) Due to industrial process, CO_2 release from calcination and SO_2 release from roasting respectively which is responsible for global warming and acid rain.

Calcination It involves heating where the volatile matter escapes leaving behind the metal oxide. In this process, the ore is heated below its melting point in the absence of air or in the limited supply of air.

e.g. $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + \underset{\substack{\text{(Carbon dioxide)}\\ \text{Responsible for}\\ \text{global warming}}}{CO_2} \uparrow$

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Roasting In this process the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal.

e.g.

$2ZnS + 3O_2 \longrightarrow 2ZnO + \underset{\text{(Sulphur dioxide) Responsible for acid rain}}{2SO_2 \uparrow}$

41 The purest form of commercial iron is **[2020, 7 Jan Shift-I]**

(a) cast iron
(b) scrap iron and pig iron
(c) wrought iron
(d) pig iron

Ans. ***(c)***

Wrought iron is the purest form of commercial iron.

42 Among the reactions (A) - (D), the reaction(s) that does/do not occur in the blast furnace during the extraction of iron is/are

(A) $CaO + SiO_2 \longrightarrow CaSiO_3$

(B) $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$

(C) $FeO + SiO_2 \longrightarrow FeSiO_3$

(D) $FeO \longrightarrow Fe + \frac{1}{2}O_2$

[2020, 8 Jan Shift-II]

(a) (C) and (D) (b) (A)
(c) (A) and (D) (d) (D)

Ans. ***(a)***

Reaction (C) and (D) do not occur in the blast furnace during the extraction of iron.

(C) $FeO + SiO_2 \longrightarrow FeSiO_3$

$\Rightarrow$ (occur in Cu metallurgy)

(D) $FeO \longrightarrow Fe + \frac{1}{2}O_2$

(not possible without reducing agent like CO) whereas, both (A) and (B) reactions occur during extraction of Fe.

(A) $CaO + SiO_2 \longrightarrow CaSiO_3$

(slag formation in blast furnace)

(B) $2Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$

$\Rightarrow$ (reduction of Fe^{3+} to Fe_3O_4)

43 **Assertion** For the extraction of iron, haematite ore is used. **[2019, 9 April Shift-II]**

Reason Heamatite is a carbonate ore of iron.

(a) Only the reason is correct.
(b) Both the assertion and reason are correct explanation for the assertion.
(c) Both the assertion and reason are correct and the reason is the correct explanation for the assertion.
(d) Only the assertion is correct.

Ans. ***(d)***

Only assertion is correct and reason is incorrect. Haematite is not a carbonate ore. It is an oxide ore, i.e. Fe_2O_3. Cast iron is extracted chiefly from its oxide ore (haematite) by heating in the presence of coke and limestone in a blast furnace.

44 The correct statement is

(a) zone refining process is used for the refining of titanium.
(b) zincite is a carbonate ore.
(c) sodium cyanide cannot be used in the metallurgy of silver.
(d) aniline is a froth stabiliser. **[2019, 10 April Shift-II]**

Ans. ***(d)***

The explanation of given statements are as follows :

(a) Zone refining process is used for the refining of B, Ga, In, Si and Ge.
Ti is refined by van Arkel method.
Thus, statement (a) is incorrect.

(b) Zincite (ZnO) is an oxide ore of Zn.
Thus, statement (b) is incorrect.

(c) NaCN is used in the hydrometallurgy of silver. It is known as Mc. Arthur Forrest process.
The reactions occuring during the process are as follows :

$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$

$4Na_2S + 2H_2O + 5O_2 \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$

$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$

Thus, statement (c) is incorrect.

(d) Aniline and cresol help in stabilising the froth in froth floatation process.
Thus, statement (d) is correct.

45 The idea of froth floatation method came from a person *X* and this method is related to the process *Y* of ores. *X* and *Y*, respectively, are **[2019, 12 April Shift-I]**

(a) fisher woman and concentration
(b) washer woman and concentration
(c) fisher man and reduction
(d) washer man and reduction

Ans. ***(b)***

The idea of froth floatation method came from a person 'washer woman' (*X*) and this method is related to the process concentration (*Y*) of ores.

This method is based upon the preferential wetting properties with the frothing agent (collector) and water.

46 The correct statement is

(a) leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate.
(b) the hall-heroult process is used for the production of aluminium and iron.
(c) pig iron is obtained from cast iron.
(d) the blistered appearance of copper during the metallurgical process is due to the evolution of CO_2. **[2019, 12 April Shift-II]**

Ans. ***(a)***

The correct statement is "leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate". Bauxite usually contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities.

Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35-36 bar pressure. Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving the impurities behind.

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq)$

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. Here, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces precipitation.

$2Na[Al(OH)_4](aq) + CO_2(g) \longrightarrow Al_2O_3 \cdot xH_2O(s) + 2NaHCO_3(aq)$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3.

$Al_2O_3 \cdot xH_2O(s) \xrightarrow{1470\ K} Al_2O_3(s) + xH_2O(g)$

47 Hall-Heroult's process is given by

(a) $ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO$
(b) $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$
(c) $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$
(d) $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$

[2019, 10 Jan Shift-I]

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Ans. *(c)*

Hall-Heroult's process is an electro-reduction process by which pure alumina (Al_2O_3) is reduced to crude Al. In this process, electrolysis of a fused mixture of Al_2O_3, $Na_3[AlF_6]$ (cryolite) and CaF_2 (fluorspar) is carried out at carbon cathode and graphite anode. The overall reaction is represented as:

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

48 The reaction that does not define calcination is

(a) $Fe_2O_3 \cdot XH_2O \xrightarrow{\Delta} Fe_2O_3 + XH_2O$

(b) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

(c) $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + 2CO_2$

(d) $2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$

[2019, 11 Jan Shift-II]

Ans. *(d)*

Calcination is one of the pyrometallurgical process, like roasting by which a concentrated ore gets converted into its oxide.

In calcination, a hydrated carbonate or bicarbonate ore or a hydrated ore is heated at lower temperature (compared to roasting) in absence of air to give its oxide as in options (a), (b) and (c). Here, volatile non-metallic oxides like H_2O, CO_2, are also produced.

Roasting is valid mainly for sulphide ores like option (d), where SO_2 gets liberated. In this reaction, calcination cannot be used.

49 In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of **[2019, 12 Jan Shift-I]**

(a) platinum
(b) carbon
(c) pure aluminium
(d) copper

Ans. *(b)*

In the Hall-Heroult's process, aluminium in formed at the cathode. The cathode is made out of carbon. In this method, Al_2O_3 is melted with cryolite, $Na_3[AlF_6]$ and electrolysed in a graphite lined steel tank, which serves as the cathode. The anode is also made of graphite.

The cell runs continuously and at intervals molten aluminium is drained from the bottom of the cell and more bauxite is added. The electrolytic reactions are as follows:

At cathode $Al^{3+} + 3e^- \longrightarrow Al$

At anode

$$C(s) + O^{2-}(melt) \longrightarrow CO(g) + 2e^-$$
$$C(s) + 2O^{2-}(melt) \longrightarrow CO_2(g) + 4e^-$$

50 The pair that does not require calcination is **[2019, 12 Jan Shift-II]**

(a) ZnO and MgO
(b) ZnO and $Fe_2O_3 \cdot xH_2O$
(c) $ZnCO_3$ and CaO
(d) Fe_2O_3 and $CaCO_3 \cdot MgCO_3$

Ans. *(a)*

The hydroxide, hydrated oxides and carbonate ores, after concentration, are subjected to calcination. In the process, the ore is heated below its melting point in the limited supply or absence of air. As the result, these are converted into their oxides.

So, among the given options, the options having either carbonates (e.g. $ZnCO_3$ and $CaCO_3 \cdot MgCO_3$) or hydrated oxide (e.g. $Fe_2O_3 \cdot xH_2O$), require calcination while pair of option (a), i.e. ZnO and MgO does not require calcination.

51 Which series of reactions correctly represent chemical relations related to iron and its compound? **[JEE Main 2014]**

(a) $Fe \xrightarrow{Dil.\ H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{Heat} Fe$

(b) $Fe \xrightarrow{O_2,\ heat} FeO \xrightarrow{dil.\ H_2SO_4} FeSO_4 \xrightarrow{Heat} Fe$

(c) $Fe \xrightarrow{Cl_2,\ heat} FeCl_3 \xrightarrow{Heat,\ air} FeCl_2 \xrightarrow{Zn} Fe$

(d) $Fe \xrightarrow{O_2,\ heat} Fe_3O_4 \xrightarrow{CO,\ 600°C} FeO \xrightarrow{CO,\ 700°C} Fe$

Ans. *(d)*

This problem involves the concept of Ellingham diagram as this diagram predicts the basis of oxidation state and stability of iron compounds.

(a) $Fe \xrightarrow{dil.\ H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{Heat} Fe$

The above given reaction series is incorrect. The correct reactions series is as follows

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$
$$H_2SO_4 + 2FeSO_4 + \frac{1}{2}O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O$$
$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3(s) + 3SO_3\uparrow$$

(b) $Fe \xrightarrow{O_2,\ heat} FeO \xrightarrow{dil.\ H_2SO_4} FeSO_4 \xrightarrow{Heat} Fe$

This reaction series is also incorrect.

The correct reaction series is

$$F \xrightarrow[\Delta]{O_2} FeO\ [\text{It could also be } Fe_2O_3 \text{ or } Fe_3O_4]$$
$$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$
$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

(c) $Fe \xrightarrow{Cl_2,\ heat} FeCl_3 \xrightarrow{Heat,\ air} FeCl_2 \xrightarrow{Zn} Fe$

The reaction of $FeCl_3$ is not possible. Thus, the above reaction series is incorrect.

(d) $Fe \xrightarrow[O_2]{\Delta} Fe_3O_4 \xrightarrow{CO,\ 600°C} FeO \xrightarrow{CO,\ 700°C} Fe$

This reaction series is correct.

52 Which one of the following ores is best concentrated by froth-floatation method? **[AIEEE 2004]**

(a) Magnetite
(b) Cassiterite
(c) Galena
(d) Malachite

Ans. *(c)*

Froth-floatation is used to concentrate sulphide ores [Galena (PbS)].

53 Aluminium is extracted by the electrolysis of **[AIEEE 2002]**

(a) alumina
(b) bauxite
(c) molten cryolite
(d) alumina mixed with molten cryolite

Ans. *(d)*

Aluminium is extracted by electrolysis of a fused mixture of alumina (2-8%), synthetic cryolite Na_3AlF_6 (80-85%), AlF_3 and fluorspar.

This makes alumina good conductor and lowers the fusion temperature also.

54 Cyanide process is used for the extraction of **[AIEEE 2002]**

(a) barium
(b) silver
(c) boron
(d) zinc

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Ans. ***(b)***

Cyanide process or Mac Arthur-Forest cyanide process

$$2Ag_2S + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH + 2S$$

Soluble silver complex is filtered and treated with zinc dust and silver gets precipitated.

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

TOPIC 3
Refining of Metals

55 In the electrolytic refining of blister copper, the total number of main impurities from the following, removed as anode mud is .....

Pb, Sb, Se, Te, Ru, Ag, Au and Pt

[2021, 31 Aug Shift-II]

Ans. ***(6)***

Impurities from blister copper deposited as anode mud contain antimony, selenium, tellurium, silver, gold and platinum.

These are basically less active metals which cannot be oxidised at anode.

56 Which refining process is generally used in the purification of low melting metals? **[2021, 27 Aug Shift-I]**

(a) Chromatographic method
(b) Liquation
(c) Electrolysis
(d) Zone refining

Ans. ***(b)***

Liquation is used for separating metals which have lower melting points than the impurities. The process is done by keeping the metal to be refined in a sloping surface of a furnace. The temperature will be maintained above the melting point of metals. Thus, pure metal melts and moves down.

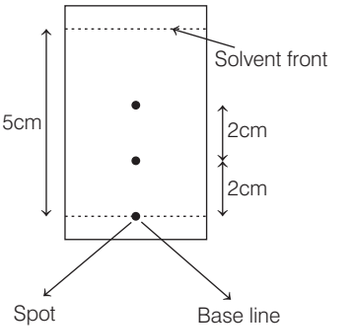
57 The method used for the purification of indium is **[2021, 25 Feb Shift-II]**

(a) van-Arkel method
(b) liquation
(c) zone refining
(d) vapour phase refining

Ans. ***(c)***

Zone refining method is very helpful for producing semiconductor and other metals of high purity,
e.g., Si, Ge, B, Ga, In etc.

58 Using the provided information in the following paper chromatogram.



Paper chromatography for compounds *A* and *B*

The calculated R_f value of *A* ..... $\times 10^{-1}$. **[2021, 25 Feb Shift-I]**

Ans. ***(4)***

The retention factor (R_f) value can be used to identify the components of a mixture (solutes).

$$R_f = \frac{\text{Distance travelled by solute}}{\text{Distance travelled by solvent front}}$$

On chromatogram, distance travelled by compound is 2 cm.

Distance travelled by solvent = 5 cm

$$\therefore \quad R_f = \frac{2}{5} = 4 \times 10^{-1}$$

59 Boron and silicon of very high purity can be obtained through

(a) liquation **[2020, 5 Sep Shift-II]**
(b) zone refining
(c) vapour phase refining
(d) electrolytic refining

Ans. ***(b)***

In zone refining the impure metal rod is electrically heated till life metal in the heated zone melts. There metal is collected at one end of the rod. Repeating the metal with the product obtained each time highly pure metal is obtained. This method is very useful for producing semiconductor and other metals with high purity.

e.g. Germanium, silicon, boron, gallium and indium etc.

60 The element that can be refined by distillation is **[2020, 6 Sep Shift-II]**

(a) nickel (b) zinc
(c) tin (d) gallium

Ans. ***(b)***

Zinc is refined by distillation.

It is used for purification of low boiling point or volatile metals, such as mercury (Hg), zinc (Zn), cadmium (Cd) etc. In this method pure metal is heated and its vapours are separately condensed in a receiver, while the pure metal distils out, impurities (non-volatile) are left behind.

61 The refining method used when the metal and the impurities have low and high melting temperatures, respectively, is **[2020, 7 Jan Shift-II]**

(a) distillation
(b) zone refining
(c) liquation
(d) vapour phase refining

Ans. ***(c)***

Liquation is used when melting points of metal and impurity are quite different.

Metal melts at a lower temperature and flows down a slope while the impurity stays as solid.

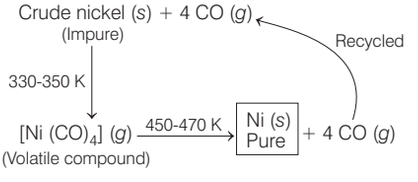
62 The Mond process is used for the **[2019, 8 April Shift-II]**

(a) purification of Ni
(b) extraction of Mo
(c) purification of Zr & Ti
(d) extraction of Zn

Ans. ***(a)***

Mond process is used in the purification of Ni. It is a vapour phase refining process.

It is based on the principle that Ni is heated in the presence of carbon monoxide to form nickel tetracarbonyl, which is a volatile complex. This complex is then decomposed by subjecting it to a higher temperature (450-470 K) to obtain pure nickel metal.



63 Match the refining methods Column I with metals Column II.

	Column I (Refining Methods)		**Column II** (Metals)
I.	Liquation	(A)	Zr
II.	Zone refining	(B)	Ni
III.	Mond process	(C)	Sn
IV.	van Arkel method	(D)	Ga

[2019, 10 April Shift-I]

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(a) I-(C) ; II-(D); III-(B) ; IV-(A)
(b) I-(B) ; II-(C); III-(D) ; IV-(A)
(c) I-(C) ; II-(A); III-(B) ; IV-(D)
(d) I-(B) ; II-(D); III-(A) ; IV-(C)

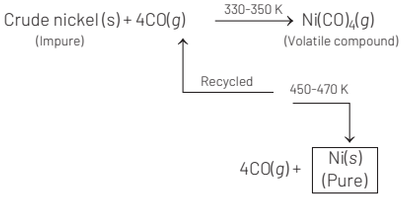
Ans. ***(a)***

Refining of crude metals results pure metals and its impurities get separated out.

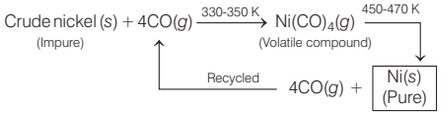
I. **Liquation** In this method low melting metals like Sn, Pb, Bi and Hg can be made to flow down through a sloping surface leaving behind the higher melting impurities on the hearth.

II. **Zone refining** The basic principle of the method is, impurities are more soluble in the molten metal than in the solid state of the metal. This method is useful to produce semiconductors and ultra-pure metals like B, Ga, In, Si and Ge.

III. **Mond process**



IV. **van Arkel method**



Here, $M = Zr, Hf, Ti$

Hence, the correct matching is

$I \rightarrow (C), II \rightarrow (D), III \rightarrow (B), IV \rightarrow (A)$.

64 The electrolytes usually used in the electroplating of gold and silver, respectively, are **[2019, 10 Jan Shift-II]**

(a) $[Au(OH)_4]^-$ and $[Ag(OH)_2]^-$
(b) $[Au(NH_3)_2]^+$ and $[Ag(CN)_2]^-$
(c) $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$
(d) $[Au(CN)_2]^-$ and $[AgCl_2]^-$

Ans. ***(c)***

Electroplating is a process of coating one metal or metal object with a very thin layer of another metal typically applying a direct electric current.

Electrolytes used in the electroplating of gold and silver are given in the table below :

			Pure metal block acts an anode by which electroplating will be done	
(a)	Gold plating	Article	Ai(S)	$Na[Au(CN)_2]$ (Sodium auro-cyanide)
(b)	Silver plating	Article	Ag(S)	$Na[Ag(CN)_2]$ (Sodium argento cyanide)

65 Which method of purification is represented by the following equation? **[AIEEE 2012]**

$$Ti(s) + 2I_2(g) \xrightarrow{523\ K} TiI_4(g) \xrightarrow{1700\ K} Ti(g) + 2I_2(g)$$

(a) Zone refining (b) Cupellation
(c) Polling (d) van-Arkel

Ans. ***(d)***

van-Arkel method is used for refining Titanium and Zirconium. This method is useful for removing volatile impurities like O_2, N_2, I_2 present in the metals of Zr and Ti.

In this method, metal iodide is formed by direct combination of metal and iodine.

The metal iodide undergo decomposition on a tungsten filament and thus, pure metal is deposited on the filament.

66 During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are **[AIEEE 2005]**

(a) Fe and Ni (b) Ag and Au (c) Pb and Zn (d) Se and Ag

Ans. ***(b)***

During electrolysis, noble metals (inert metals) like Ag, Au and Pt are not affected and separate as anode mud from the impure anode.

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15

Hydrogen

TOPIC 1

Preparation and Properties of Hydrogen

01 Which one of the following statements is incorrect ?

[2021, 31 Aug Shift-II]

(a) Atomic hydrogen is produced when H_2 molecules at a high temperature are irradiated with UV radiation.

(b) At around 2000 K, the dissociation of dihydrogen into its atoms is nearly 8.1%.

(c) Bond dissociation enthalpy of H_2 is highest among diatomic gaseous molecules which contain a single bond .

(d) Dihydrogen is produced on reacting zinc with HCl as well as NaOH(*aq*).

Ans. ***(b)***

Statement (b) is incorrect. The corrected statement is :

At around 2000 K, the dissociation of dihydrogen into its atoms is only ~0.081%.

Bond dissociation enthalpy of H_2 molecule is highest due to very strong attraction between the atoms.

$$Zn + 2HCl \longrightarrow H_2 + ZnCl_2$$

$$Zn + NaOH \longrightarrow Na_2ZnO_2 + H_2$$

H—H bond dissociate by increasing temperature and shining UV light.

02 The number of neutrons and electrons, respectively, present in the radioactive isotope of hydrogen is **[2021, 27 July Shift-II]**

(a) 1 and 1 (b) 3 and 1
(c) 2 and 1 (d) 2 and 2

Ans. ***(c)***

Radioactive isotope of hydrogen is tritium. It is represented as follows

$$\text{Atomic mass} \longrightarrow 3$$
$$\text{Atomic number} \longrightarrow 1 \quad T$$

We know that, for neutral element

Atomic number (Z) = Number of protons (n_p) = Number of electrons (n_e) = 1

Atomic mass (A) = Number of neutrons + Number ofprotons

$$3 = n_n + n_p$$
$$3 = n_n + 1$$
$$3 - 1 = n_n \Rightarrow n_n = 2$$

03 Isotope(s) of hydrogen which emits low energy β^- particles with $t_{1/2}$ value > 12 years is/are **[2021, 22 July Shift-II]**

(a) protium
(b) tritium
(c) deuterium
(d) deuterium and tritium

Ans. ***(b)***

Tritium is the only isotope of hydrogen which is radioactive.

Tritium has a half-life of 12.3 yr and it emits low energy β-particles (β^-).

04 The single largest industrial application of dihydrogen is **[2021, 20 July Shift-II]**

(a) manufacture of metal hydrides
(b) rocket fuel in space research
(c) in the synthesis of ammonia
(d) In the synthesis of nitric acid

Ans. ***(c)***

Dihydrogen is used as rocket fuel in space research. Metal react with hydrogen gas to form metal hydrides.

$$\text{Metal} + H_2 \longrightarrow \text{Metal hydrides}$$

H_2 also used for synthesis of nitric acid (HNO_3).

Hydrogen gas react with nitrogen dioxide to form water and nitrous oxide.

$$H_2(g) + NO_2(g) \longrightarrow H_2O(g) + NO(g)$$

Nitrogen dioxide reacts with water to form nitric acid and nitrous oxide.

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

The single largest industrial application of dihydrogen in the synthesis of ammonia (Haber's process).

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

05 Dihydrogen of high purity (> 99.95%) is obtained through **[2020, 6 Sep Shift-II]**

(a) the reaction of Zn with dilute HCl
(b) the electrolysis of acidified water using Pt electrodes
(c) the electrolysis of brine solution
(d) the electrolysis of warm $Ba(OH)_2$ solution using Ni electrodes.

Ans. ***(d)***

Electrolysis of warm aqueous $Ba(OH)_2$ solution between nickel electrodes is a commercial method to obtain highly pure (> 99.95%) dihydrogen.

In the presence of $Ba(OH)_2$, water dissociates into ions easily and quickly and H^+ ions are produced, which go on cathode, gets discharged there and liberate hydrogen gas.

06 The equation that represents the water-gas shift reaction is **[2020, 5 Sep Shift-I]**

(a) $C(s) + H_2O(g) \xrightarrow{1270\,K} CO(g) + H_2(g)$

(b) $2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\,K} 2CO(g) + 4N_2(g)$

(c) $CO(g) + H_2O(g) \xrightarrow[\text{Catalyst}]{673\,K} CO_2 + H_2(g)$

(d) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\,K} CO(g) + 3H_2(g)$

Ans. ***(c)***

In water gas shift reaction, hydrogen gas is produced economically by the reaction of carbon monoxide with water vapour at

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673 K in presence of iron, cromium and copper zinc catalyst.

$$CO + H_2O(g) \xrightarrow[\Delta]{\text{Catalyst}} CO_2(g) + H_2(g)$$

07 5 g of zinc is treated separately with an excess of
(1) dilute hydrochloric acid and
(2) aqueous sodium hydroxide.
The ratio of the volume of H_2 evolved in these two reactions is
[2020, 9 Jan Shift-II]

(a) 2 : 1 (b) 1 : 1
(c) 1 : 4 (d) 1 : 2

Ans. ***(b)***

Treatment of zinc with an excess of dil. HCl and aqueous sodium hydroxide are as follows :

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2 \uparrow$$
$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2 \uparrow$$

In both cases, 1 mol Zn gives 1 mol H_2, ratio is 1 : 1.

08 The metal that gives hydrogen gas upon treatment with both acid as well as base is
[2019, 12 April Shift-I]

(a) magnesium (b) mercury
(c) zinc (d) iron

Ans. ***(c)***

Metal that gives hydrogen gas upon treatment with both acid as well as base is zinc.

Hence, it is amphoteric in nature.
Reactions involved are as follows:

$$Zn + \text{Dil. } NaOH \longrightarrow Na_2ZnO_2 + H_2 \uparrow$$
$$Zn + 2HCl(\text{dil.}) \longrightarrow ZnCl_2 + H_2 \uparrow$$

09 The isotopes of hydrogen are
(a) deuterium and tritium only
(b) protium and deuterium only
(c) protium, deuterium and tritium
(d) tritium and protium only
[2019, 9 Jan Shift-I]

Ans. ***(c)***

There are three known isotopes of hydrogen, each possessing an atomic number 1 and atomic masses 1, 2 and 3 respectively. These are named as protium (^1H), deuterium (^2H or D) and tritium (^3H or T)

The most common isotope is the ordinary hydrogen usually called protium. It consists of one proton in the nucleus and an electron revolving around it.

The second isotope of hydrogen is called heavy hydrogen or deuterium. It consists of one proton and one neutron in the nucleus and an electron revolving around it. The third isotope of hydrogen is called tritium. It consists of one proton and two neutrons in the nucleus and an electron revolving around it.

10 The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are
[2019, 10 Jan Shift-I]

(a) 2 and 1
(b) 3 and 2
(c) 2 and 0
(d) 3 and 1

Ans. ***(d)***

Hydrogen has three isotopes:

	^1_1H Protium (P)	^2_1H Deuterium (D)	^3_1H Tritium (T)
p	1	1	1
n	0	1	2
n/p	0	1	2

Only tritium (T) is radioactive, because of its very high $\frac{n}{p}$ value, $\left(\frac{n}{p}=2\right)$.

11 Very pure hydrogen (99.9) can be made by which of the following processes?
[AIEEE 2012]

(a) Reaction of methane with steam
(b) Mixing natural hydrocarbons of high molecular weight
(c) Electrolysis of water
(d) Reaction of salts like hydrides with water

Ans. ***(d)***

Hydrides are instant source of hydrogen of higher purity. They react with H_2O forming H_2 gas.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

12 In context with the industrial preparation of hydrogen from water gas ($CO + H_2$), which of the following is the correct statement ?
[AIEEE 2008]

(a) CO and H_2 are fractionally separated using differences in their densities
(b) CO is removed by absorption in aqueous Cu_2Cl_2 solution
(c) H_2 is removed through occlusion with Pd
(d) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali.

Ans. ***(d)***

CO is oxidised to CO_2 with steam in the presence of a catalyst followed by the absorption of CO_2 in alkali

$$CO + H_2 \xrightarrow[\text{catalyst}]{\text{Steam}} CO_2 + 2H_2$$
$$\downarrow KOH$$
$$K_2CO_3$$

13 Which of the following could act as a propellant for rockets ?
[AIEEE 2003]

(a) Liquid hydrogen + liquid nitrogen
(b) Liquid oxygen + liquid argon
(c) Liquid hydrogen + liquid oxygen
(d) Liquid nitrogen + liquid oxygen

Ans. ***(c)***

Liquid hydrogen and liquid oxygen are good fuels.

TOPIC 2
Hydrides and Water

14 Which one of the following methods is most suitable for preparing deionised water?
[2021, 26 Aug Shift-I]

(a) Synthetic resin method
(b) Clark's method
(c) Calgon's method
(d) Permutit method

Ans. ***(a)***

Synthetic resin method is most suitable for preparing deionised water. Deionised water is obtained by passing water through cation exchange and an anion exchange resin.

15 The functional groups that are responsible for the ion-exchange property of cation and anion exchange resins, respectively, are
[2021, 17 March Shift-II]

(a) — SO_3H and —NH_2
(b) —SO_3H and —COOH
(c) — NH_2 and —COOH
(d) —NH_2 and —SO_3H

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Ans. ***(a)***

The functional group responsible for the ion-exchange property of cation is —SO_3H and that of anion is —NH_2.

Cation resins attract positively charged ions and contain acidic group like —SO_3H or —COOH groups. While anion resins attract negatively charged ions and contains basic groups like —NH_2.

16 Calgon is used for water treatment. Which of the following statement is not true about Calgon? **[2021, 26 Feb Shift-II]**

(a) Calgon contains the 2nd most abundant element by weight in the Earth's crust.
(b) It is polymeric compound and is water soluble.
(c) It is also known as Graham's salt.
(d) It does not remove Ca^{2+} ion by precipitation.

Ans. ***(a)***

Calgon is used to remove permanent hardness of water by removing cation Mg^{2+}.

Calgon is not an element, it is a compound. The 2nd most abundant element by weight in the Earth's crust is silicon (Si). So, the statement in option (a) is not true.

Calgon is sodium hexametaphosphate $(NaPO_3)_6$ or $Na_2[Na_4(PO_3)_6]$. It is a polymeric water soluble compound. It is also named as Graham's salt.

Mg^{2+} of hard water is removed as

$$Na_2[Na_4(PO_4)_3] + 2Mg^{2+}(aq) \longrightarrow \overset{\text{Calgon}}{Na_2[Mg_2(PO_3)_6](s)} + 4Na^+(aq)$$

Ca^{2+} ion cannot be removed by calgon as Ca^{2+} is larger in size than Mg^{2+}.

So, the statement of option (b), (c) and (d) are true.

17 The one that is not suitable for the removal of permanent hardness of water is **[2020, 5 Sep Shift-II]**

(a) Clark's method
(b) Ion-exchange method
(c) Calgon's method
(d) Treatment with sodium carbonate

Ans. ***(b)***

Temporary hardness of water is removed by Clark's method and boiling. In method a calculated quality of milk of lime $[Ca(OH)_2]$ is added to the temporary hard water. This treatment converses the soluble bicarbonates into insoluble carbonates which get precipitated and can be removed by filteration. While permanent hardners of water is removed by treatment with sodium carbonate (Na_2CO_3), Calogon method and ion exchange method.

18 In comparison to the zeolite process for the removal of permanent hardness, the synthetic resins method is **[2020, 7 Jan Shift-I]**

(a) more efficient as it can exchange only cations
(b) less efficient as it exchanges only anions
(c) less efficient as the resins cannot be regenerated
(d) more efficient as it can exchange both cations as well as anions

Ans. ***(d)***

Zeolites exchange their Na^+ ions with Ca^{2+} or Mg^{2+} in hard water. But, they can't exchange anions.

$$2NaZ(s) + \underset{\text{From hard water}}{Mg^{2+}(\text{or } Ca^{2+})(aq)} \longrightarrow MgZ_2(s)\ (\text{or } CaZ_2)(s) + 2Na^+(aq)$$

In synthetic resin method, all types cations (Na^+, Ca^{2+}, Mg^{2+} etc.) and anions (Cl^-, SO_4^{2-} etc.) can be removed.

Thus, this method is more efficient than zeolite process.

19 The correct statements among (a) to (d) are : **[2019, 10 April Shift-II]**

1. Saline hydrides produce H_2 gas when reacted with H_2O.
2. Reaction of $LiAlH_4$ with BF_3 leads to B_2H_6.
3. PH_3 and CH_4 are electron rich and electron precise hydrides, respectively.
4. HF and CH_4 are called as molecular hydrides.

(a) (1), (2), (3) and (4)
(b) (1), (2) and (3) only
(c) (3) and (4) only
(d) (1), (3) and (4) only

Ans. ***(a)***

The explanation of given statements are as follows :

1. Saline or ionic hydrides produce H_2 with H_2O.

$$\overset{\oplus}{M}H + \overset{\ominus}{H_2O} \longrightarrow H_2\uparrow + MOH$$

Thus, statement (1) is correct.

2. $3LiAlH_4 + 4BF_3 \xrightarrow{\text{Ether}} \underset{\text{(Diborane)}}{2B_2H_6} + 3LiF + 3AlF_3$

Thus, statement (2) is correct.

3. PH_3 and CH_4 are covalent hydrides and in both of the hydrides, octet of P and C have been satisfied. But P in PH_3 has one lone pair of electrons and C in CH_4 does not have so PH_3 (group 15) and CH_4 (group 14) are electron rich and electron precise hydrides, respectively.

Thus, statement (3) is correct.

4. HF and CH_4 are called as molecular hydrides because of their discrete and sterically symmetrical structure.

Thus, statement (4) is also correct.

20 The temperary hardness of a water sample is due to compound *X*. Boiling this sample converts *X* to compound *Y*. *X* and *Y*, respectively, are **[2019, 12 April Shift-II]**

(a) $Mg(HCO_3)_2$ and $Mg(OH)_2$
(b) $Ca(HCO_3)_2$ and $Ca(OH)_2$
(c) $Mg(HCO_3)_2$ and $MgCO_3$
(d) $Ca(HCO_3)_2$ and CaO

Ans. ***(a)***

The temperary hardness of a water sample is due to compound *X* [i.e. $Mg(HCO_3)_2$]. Boiling of this sample converts *X* [i.e. $Mg(HCO_3)_2$] to compound *Y* [i.e. $Mg(OH)_2$]. Generally, temporary hardness is due to presence of magnesium and calcium hydrogen carbonates. It can be removed by boiling. During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ changed to insoluble $CaCO_3$. These precipitates can be removed by filteration.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

21 What is reason of temporary hardness of water? **[2019, 9 Jan Shift-II]**

(a) Na_2SO_4 (b) $CaCl_2$
(c) NaCl (d) $Ca(HCO_3)_2$

Ans. ***(d)***

Temporary hardness of water is due to presence of soluble $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$

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Permanent hardness of water is due to the presence of $CaCl_2$ or $CaSO_4$ or $MgCl_2$ or $MgSO_4$.

Temporary hardness of water is also called carbonate hardness which can be easily removed by boiling or by treatment with $Ca(OH)_2$ (Clark's method).

22 Match the following items in Column I with the corresponding items in Column II.

	Column I		Column II
(i)	$Na_2CO_3 \cdot 10H_2O$	A.	Portland cement ingredient
(ii)	$Mg(HCO_3)_2$	B.	Castner-Kellner process
(iii)	NaOH	C.	Solvay process
(iv)	$Ca_3Al_2O_6$	D.	Temporary hardness

[2019, 11 Jan Shift-II]

(a) (i) - (D); (ii) - (A); (iii) - (B); (iv) - (C)
(b) (i) - (B); (ii) - (C); (iii) - (A); (iv) - (D)
(c) (i) - (C); (ii) - (B); (iii) - (D); (iv) - (A)
(d) (i) - (C); (ii) - (D); (iii) - (B); (iv) - (A)

Ans. ***(d)***

(i) Washing soda ($Na_2CO_3 \cdot 10H_2O$) is manufactured in Solvay process. In this method, CO_2 gas is passed through a conc. solution of NaCl saturated with NH_3. It gives ammonium carbonate followed by ammonium hydrogen carbonate.

The obtained NH_4HCO_3 is treated with solution of NaCl which result in the formation of $NaHCO_3$. The crystal obtained are heated to obtain Na_2CO_3.

$$NaCl + NH_3 + CO_2 + H_2O \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \xrightarrow[-H_2O,\ CO_2]{\Delta} Na_2CO_3$$

$$\xrightarrow{\text{Crystallisation}} Na_2CO_3 \cdot 10H_2O$$

(ii) $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ cause temporary hardness to water that can be easily removed by boiling.

(iii) NaOH is manufactured by Castner-Kellner process.

In this reaction, Na amalgam flows out and treated with water to give NaOH and H_2 gas. During electrolysis, hydrogen is evolved at cathode and chlorine is evolved at anode, which are the by product of this process.

(iv) Portland cement constitutes, tricalcium aluminosilicate, $3CaO \cdot Al_2O_3 \cdot SiO_2$, i.e. $Ca_3Al_2O_6 \cdot SiO_2$.

23 The recommended concentration of fluoride ion in drinking water is up to 1 ppm as fluoride ion is required to make teeth enamel harder by converting $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ to : **[JEE Main 2018]**

(a) $[CaF_2]$
(b) $[3(CaF_2) \cdot Ca(OH)_2]$
(c) $[3Ca_3(PO_4)_2 \cdot CaF_2]$
(d) $[3\{Ca_3(PO_4)_2\} \cdot CaF_2]$

Ans. ***(c)***

Fluoride ions help in making teeth enamel harder by converting $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ i.e. Hydroxy apatite to $[3Ca_3(PO_4)_2 \cdot CaF_2]$ i.e., Fluorapatite (Harder teeth enamel) *via* following reaction:

$$[3Ca_3(PO_4)_2 \cdot Ca(OH)_2] + \underset{\text{From drinking water}}{2F^-} \longrightarrow [3Ca_3(PO_4)_2 \cdot CaF_2] + 2OH^-$$

24 Which one of the following statements about water is false? **[JEE Main 2016]**

(a) Water can act both as an acid and as a base
(b) There is extensive intramolecular hydrogen bonding in the condensed phase
(c) Ice formed by heavy water sinks in normal water
(d) Water is oxidised to oxygen during photosynthesis

Ans. ***(b)***

There is extensive intermolecular H-bonding in the condensed phase.

25 Which one of the following processes will produce hard water? **[AIEEE 2003]**

(a) Saturation of water with $CaCO_3$
(b) Saturation of water with $MgCO_3$
(c) Saturation of water with $CaSO_4$
(d) Addition of Na_2SO_4 to water

Ans. ***(c)***

Alkaline earth metal salts causes hardness of water. Temporary hardness is caused by soluble Ca and Mg hydrogen carbonates. Whereas calcium and magnesium soluble sulphates and chlorides cause permanent hardness of water.

TOPIC 3
Heavy Water and H_2O_2

26 Hydrogen peroxide reacts with iodine in basic medium to give **[2021, 1 Sep Shift-II]**

(a) IO_4^- (b) IO^- (c) I^- (d) IO_3^-

Ans. ***(c)***

Hydrogen peroxide reacts with iodine in basic medium to give I^- (Iodide ion).

$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$

27 The oxide that gives H_2O_2 most readily on treatment with H_2O is **[2021, 27 Aug Shift-II]**

(a) PbO_2 (b) Na_2O_2
(c) SnO_2 (d) $BaO_2 \cdot 8H_2O$

Ans. ***(b)***

When sodium peroxide reacts with water,
it is hydrolysed and forms sodium hydroxide and hydrogen peroxide.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

The reaction is highly exothermic.
Therefore, the option (b) is correct.

28 Given below are two statements : One is labelled as Assertion A and other is labelled as Reason R.

Assertion (A) The dihedral angles in H_2O_2 in gaseous phase is 90.2° and in solid phase is 111.5°.

Reason (R) The change in dihedral angle in solid and gaseous phase is due to the difference in the intermolecular forces.

Choose the most appropriate answer from the options given below for A and R. **[2021, 20 July Shift-I]**

(a) A is correct but R is not correct.
(b) Both A and R are correct but R is not the correct explanation of A.
(c) Both A and R are correct and R is the correct explanation of A.
(d) A is not correct but R is correct.

Ans. ***(d)***

On the basis of structure,

(a) H_2O_2 structure in gas phase, dihedral angle is 111.5°.
(b) H_2O_2 structure in solid phase at 110 K, dihedral angle is 90.2°.

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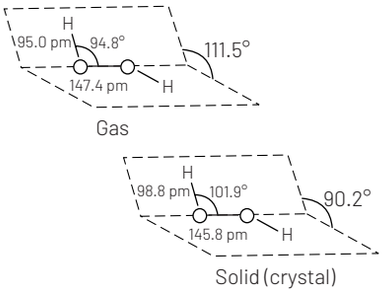


Whereas, the change in dihedral angle in solid and gaseous phase is due to the difference in the intermolecular forces.

Hence, A is not correct but R is correct.

29 Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Heavy water is used for the study of reaction mechanism.

Reason (R) The rate of reaction for the cleavage of O—H bond is slower than that of O—D bond.

Choose the most appropriate answer from the options given below.

[2021, 26 Aug Shift-II]

(a) Both (A) and (R) are true but (R) is not the correnct explanation of (A).
(b) Both (A) and (R) are true and (R) is the correct explanation of (A).
(c) (A) is false but (R) is true.
(d) (A) is true but (R) is false.

Ans. ***(d)***

Assertion is true but Reason is false.

Heavy water (D_2O) is used as a moderator in nuclear reactor and in exchange reaction for study of reaction mechanisms.

As bond energy of O—H < Bond energy of O—D. Reaction rate for cleavage of O—H bond is faster than O—D bond.

30 The incorrect statement(s) about heavy water is (are)

(A) used as a moderator in nuclear reactor.
(B) obtained as a by-product in fertiliser industry.
(C) used for the study of reaction mechanism.
(D) has a higher dielectric constant than water.

Choose the correct answer from the options given below :

[2021, 17 March Shift-I]

(a) (B) only
(b) (C) only
(c) (D) only
(d) (C) and (D) only

Ans. ***(c)***

Dielectric constant of water is greater than heavy water (D_2O).

A. It is widely used as moderator in nuclear reactors.
B. It can be prepared as a by-product in some fertiliser industries.
C. It is used in exchange reactions for the study of the reaction mechanism.
D.

Species	Dielectric constant (C^2 / Nm^2)
D_2O	78.06
H_2O	78.39

31 The correct statements about H_2O_2 are

(A) used in the treatment of effluents.
(B) used as both oxidising and reducing agents.
(C) the two hydroxyl groups lie in the same plane.
(D) miscible with water.

Choose the correct answer from the options given below.

[2021, 16 March Shift-II]

(a) (A), (B), (C) and (D)
(b) (A), (B) and (D)
(c) (B), (C) and (D)
(d) (A), (C) and (D)

Ans. ***(b)***

H_2O_2 act as both oxidising and reducing agent.

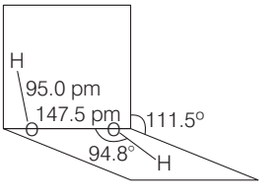
Oxygen is present in –1 oxidation state, so it can be oxidised to O_2 as well as reduced to water.

$$\underset{\text{Oxidising agent}}{H_2\overset{-1}{O_2}} \longrightarrow H_2\overset{-2}{O} \quad \text{(Reduction)}$$

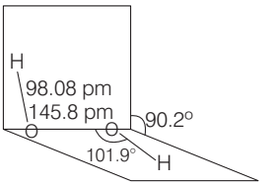
$$\underset{\text{Reducing agent}}{H_2\overset{-1}{O_2}} \longrightarrow \overset{0}{O_2} \text{ (Oxidation)}$$

H_2O_2 is miscible with water due to intermolecular H-bonding.

Due to open book like structure both —OH groups are not in same plane and hence, H_2O_2 is non-planar.



(a) Gas phase



(b) Solid phase

(a) H_2O_2 structure in gas phase, dihedral angle is 111.5°.
(b) H_2O_2 structure in solid phase at 110 K, dihedral angle is 90.2°.

H_2O_2 used in treatment of effluents.

32 Given below are two statements.

Statement I H_2O_2 can act as both oxidising and reducing agent in basic medium.

Statement II In the hydrogen economy, the energy is transmitted in the form of dihydrogen. In the light of the above statements, choose the correct answer from the options given below : **[2021, 16 March Shift-I]**

(a) Both statement I and statement II are false.
(b) Both statement I and statement II are true.
(c) Statement I is true but statement II is false.
(d) Statement I is false but statement II is true.

Ans. ***(b)***

H_2O_2 can act as both oxidising and reducing agent in basic medium as in hydrogen peroxide oxygen is present in intermediate-1 oxidation state. So, it can get oxidised to O_2 and reduced to water.

$$\underset{\substack{-1\\ \text{Oxidising agent}}}{H_2O_2} \longrightarrow \underset{-2}{H_2O} \text{(reduction)}$$

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$\underset{\text{Reducing agent}}{\underset{-1}{H_2O_2}} \longrightarrow \underset{0}{O_2}$ (oxidation)

In the hydrogen economy, the energy is transmitted in the form of dihydrogen and not as electric power.

So, both statement I and statement II are true.

33 Statements about heavy water are given below.

A. Heavy water is used in exchange reactions for the study of reaction mechanisms.
B. Heavy water is prepared by exhaustive electrolysis of water.
C. Heavy water has higher boiling point than ordinary water.
D. Viscosity of H_2O is greater than D_2O.

Which of the given statements are correct? **[2021, 26 Feb Shift-I]**

(a) A, B and C (b) Only A and B
(c) Only A and D (d) Only A and C

Ans. ***(a)***

Statement A is true. Heavy water (D_2O) is used in exchange reactions as a tracer compound for the study of reaction mechanisms.

e.g. $NaOH + D_2O \longrightarrow NaOD + HDO$

Statement B is true. Heavy water is prepared by prolonged exhaustive (multi-stage) electrolysis of ordinary water (H_2O) containing NaOH.

Statement C is true. Heavy water has higher boiling point (374.4K) than ordinary water (373K).

Statement D is false. Because viscosity (in centipoise) of D_2O is greater (1.107) than H_2O (0.8903).

So, statements A, B and C are correct (option-a).

34 (A) $HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$

(B) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$

Choose the correct option. **[2021, 24 Feb Shift-I]**

(a) H_2O_2 acts as oxidising agent in equations (A) and (B).
(b) H_2O_2 acts as reducing agent in equations (A) and (B).
(c) H_2O_2 act as oxidising and reducing agent respectively in equations (A) and (B).
(d) H_2O_2 acts as reducing and oxidising agent respectively in equations (A) and (B).

Ans. ***(b)***

In equation (A), HOCl undergoes reduction in presence of H_2O_2.

$\overset{\text{Reduction}}{\underset{(+1) \qquad\qquad (-1)}{HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2}}$

Here, oxidation state of Cl changes from +1 to –1
(i.e. reduces)

$\therefore H_2O_2$ act as reducing agent I_2 reduces to I^- in presence of H_2O_2.

In equation (B),

$\overset{\text{Reduction}}{\underset{0 \quad +1 \qquad\qquad -1 \quad +2}{I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2}}$

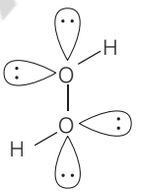
Here oxidation state of iodine decreases (from 0 to –1)

$\therefore H_2O_2$ act as reducing agent in both the equations.

35 Hydrogen peroxide, in the pure state, is **[2020, 5 Sep Shift-II]**

(a) non-planar and almost colourless
(b) linear and blue in colour
(c) linear and almost colourless
(d) planar and blue in colour

Ans. ***(a)***



Hydrogen peroxide is a colour less viscous liquid but in large quantity it appears pale blue liquid.

Hydrogen peroxide is a mild antiseptic used on the skin to prevent infections.

36 Among statements (*A*) - (*D*), the correct ones are

(A) decomposition of hydrogen peroxide gives dioxygen.
(B) like hydrogen peroxide, compounds, such as $KClO_3$, $Pb(NO_3)_2$ and $NaNO_3$ when heated liberate dioxygen.
(C) 2-ethylanthraquinone is useful for the industrial preparation of hydrogen peroxide.
(D) hydrogen peroxide is used for the manufacture of sodium perborate. **[2020, 7 Jan Shift-II]**

(a) (A), (B) and (C) only
(b) (A), (B), (C) and (D)
(c) (A), (C) and (D) only
(d) (A) and (C) only

Ans. ***(b)***

The complete chemical equations for the given reactions are as follows :

(A) $H_2O_2 \xrightarrow{\Delta} H_2O + \frac{1}{2}O_2$

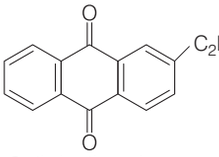
Thus, statement (A) is correct

(B) $KClO_3 \xrightarrow{\Delta} KCl + \frac{3}{2}O_2$

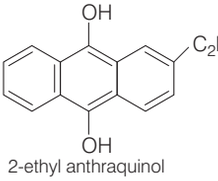
$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + \frac{1}{2}O_2$

$NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$

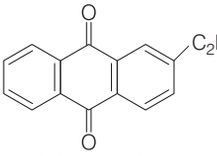
Thus, statement (B) is correct.

(C)  + H_2 $\longrightarrow$

2-ethyl anthraquinone

 + O_2 $\longrightarrow$

2-ethyl anthraquinol

 + H_2O_2

2-ethyl anthraquinone regenerated

Thus, statement (C) is also correct.

(D) $2NaBO_2 + 2H_2O_2 \longrightarrow Na_2B_2O_4(OH)_4$ or $Na_2H_4B_2O_8$ (sodium perborate)

Statement (D) is also correct.

37 The chemical nature of hydrogen peroxide is **[2019, 10 Jan Shift-I]**

(a) oxidising and reducing agent in both acidic and basic medium
(b) oxidising and reducing agent in acidic medium, but not in basic medium
(c) reducing agent in basic medium, but not in acidic medium
(d) oxidising agent in acidic medium, but not in basic medium

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Ans. *(a)*

H_2O_2 can act as both oxidising and reducing agents in both acidic and basic medium.

H_2O_2 as oxidising agent

In acidic medium :

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$

In basic medium :

$$H_2O_2 + 2\overline{O}H + 2e^- \longrightarrow 2H_2O + 2O^{2-}$$

H_2O_2 as reducing agent

In acidic medium :

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

In basic medium :

$$H_2O_2 + 2OH^- \longrightarrow O_2 + 2H_2O + 2e^-$$

38 The correct statements among (I) to (IV) regarding H_2 as a fuel are :

I. It produces less pollutants than petrol.

II. A cylinder of compressed dihydrogen weights ~ 30 times more than a petrol tank producing the same amount of energy.

III. Dihydrogen is stored in tanks of metal alloys like $NaNi_5$.

IV. On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively.

[2019, 11 Jan Shift-I]

(a) I, II and III only
(b) II, III and IV only
(c) II and IV only
(d) I and III only

Ans. *(a)*

(I) H_2 is a 100% pollution free fuel. So, option (I) is correct.

(II) Molecular weight of $H_2(2u) = \frac{1}{29} \times$ molecular weight of butane, C_4H_{10} (LPG) [58u].

So, compressed H_2 weighs ~ 30 times more than a petrol tank and option (b) is correct.

(III) $NaNi_5$, $Ti\text{-}TiH_2$ etc. are used for storage of H_2 in small quantities. Thus, option (c) is correct.

(IV) On combustion values of energy released per gram of liquid dihydrogen (H_2) : 142 kJ g^{-1}, and for LPG : 50 kJ g^{-1}. So, option (d) is incorrect.

39 A metal on combustion in excess air forms *X*. *X* upon hydrolysis with water yields H_2O_2 and O_2 along with another product. The metal is

(a) Li (b) Mg
(c) Rb (d) Na

[2019, 12 Jan Shift-I]

Ans. *(c)*

Metal (*A*) is rubidium (Rb). In excess of air, it forms RbO_2 (*X*). *X* is a superoxide that have O_2^- ion. It is due to the stabilisation of large anion by large cations through lattice energy effects. RbO_2 (*X*) gets easily hydrolysed by water to form the hydroxide, H_2O_2 and O_2.

The reaction involved are as follows:

$$Rb + O_2 \longrightarrow \underset{(X)}{RbO_2} \quad \text{(superoxide)}$$

$$\underset{(X)}{2RbO_2} + 2H_2O \longrightarrow 2RbOH + H_2O_2 + O_2$$

40 The volume strength of 1 M H_2O_2 is (Molar mass of H_2O_2 = 34 g mol^{-1})

(a) 16.8 (b) 22.4
(c) 11.35 (d) 5.6

[2019, 12 Jan Shift-II]

Ans. *(c)*

Concentration of H_2O_2 is expressed in terms of volume strength, i.e. "volume of O_2 liberated by H_2O_2 at NTP". Molarity is connected to volume strength as :

$$\text{Molarity}\,(M) = \frac{x}{11.2} \text{ or } x = \text{Molarity} \times 11.2$$

where, x = volume strength

So, for 1 M H_2O_2

$$x = 1 \times 11.2 = 11.2$$

Among the given options, 11.35 is nearest to 11.2.

41 Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively.

(a) ($H_2O + O_2$) and H_2O **[JEE Main 2018]**
(b) ($H_2O + O_2$) and ($H_2O + OH^-$)
(c) H_2O and ($H_2O + O_2$)
(d) H_2O and ($H_2O + OH^-$)

Ans. *(c)*

Both reactions in their complete format are written below

(i) In acidic medium,

$$[Fe^{2+}(CN)_6]^{4-} + H_2\overset{-1}{O_2} + 2H^+ \longrightarrow [Fe^{3+}(CN)_6]^{3-} + 2H_2\overset{-2}{O}$$

(ii) In alkaline medium,

$$[Fe^{3+}(CN)_6]^{3-} + H_2\overset{-1}{O_2} + 2OH^- \longrightarrow [Fe^{2+}(CN)_6]^{4-} + O_2 + 2H_2O$$

Hence, H_2O (for reaction (i)) and $O_2 + H_2O$ (for reaction (ii)) are produced as by product.

42 From the following statements regarding H_2O_2, choose the incorrect statement. **[JEE Main 2015]**

(a) It can act only as an oxidising agent
(b) It decomposed on exposure to light
(c) It has to be stored in plastic or wax lined glass bottles in dark
(d) It has to be kept away from dust

Ans. *(a)*

H_2O_2 acts as an oxidising as well as reducing agent, because oxidation number of oxygen in H_2O_2 is -1. So, it can be oxidised to oxidation state 0 or reduced to oxidation state –2.

H_2O_2 decomposes on exposure to light. So, it has to be stored in plastic or wax lined glass bottles in dark for the prevention of exposure. It also has to be kept away from dust.

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16

s-Block Elements

TOPIC 1

Group 1 Elements (Alkali Metals)

01 Given below are two statements : One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Lithium salts are hydrated.

Reason (R) Lithium has higher polarising power than other alkali metal group members.

In the light of the above statements, choose the most appropriate answer from the options given below

[2021, 31 Aug Shift-II]

(a) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(b) (A) is true but (R) is not true

(c) (A) is false but (R) is ture.

(d) Both (A) and (R) are true (R) is the correct explanation of (A).

Ans. ***(a)***

Both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

Lithium ions have smaller size as compared to other ions of the group.

Hence, it has greater value of charge to radius ratio and polarising power.

Among alkali metals ions, Li has smallest size due to which it can easily polarise water molecule. LiCl contains 2 water molecules per mole. However, due to bigger size of other alkali metals, they cannot easily polarise water molecules.

02 Choose the correct statement from the following. **[2021, 27 Aug Shift-II]**

(a) The standard enthalpy of formation for alkali metal bromide becomes less negative on descending the group.

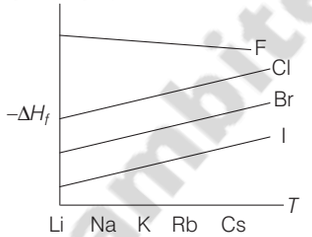
(b) The low solubility of CsI in water is due to its high lattice enthalpy.

(c) Among the alkali metal halides, LiF is least soluble in water.

(d) LiF has least negative standard enthalpy of formation among alkali metal fluorides.

Ans. ***(c)***

The ΔH_f of alkali metal halides is shown through this graph.



This graph shows that formation of metal halide is negative, i.e. energy is released during the formation of metal halides.

(A)

M—F
M—Cl
M—Br
M—I ↓

On moving down the group, the size of halogens increase which results in the lengthening of bond, making the bond weaker. Therefore, ΔH_f is less negative on moving down the group as the stability of metal halide decreases down the group.

(B)

Li—X
Na—X
K—X
Rb —X ↓

On moving down the group, the electropositivity of metal increases making the attraction between the oppositely charged ions even stronger, thus increasing the strength of bond. Increase in strength is more than the weakness produced due to lengthening of bond because of increase in size of metal ions down the group. This makes ΔH_f more negative on moving down the group.

Option (a) is incorrect, due to reason produced in (B).

Option (b) is incorrect. As CsI has $Cs^{\oplus}$ and $I^{\ominus}$ an constituent ions and both the ions are larger in size. The lattice enthalpy is not so high as shown in graph. But it has low solubility due to less hydration energy released when hydration of larger ions takes place.

Option (c) is correct. As LiF has highest lattice enthalpy as shown in graph. This is due to the size of ions that is smallest in their respective groups. Smaller is the size, shorter is the bond length and stronger is the bond. The energy required is break the bond and release the constituents ions is more than the energy released in the hydration of ions. So, LiF is least soluble in water.

Option (d) is incorrect. LiF has most negative enthalpy in all metal fluorides as shown in graph.

03 The ratio of number of water molecules in Mohr's salt and potash alum is ..... $\times 10^{-1}$.

(Integer answer)

[2021, 26 Aug Shift-I]

Ans. ***(2.5)***

Formula for Mohr's salt is

$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$.

$\therefore$ Number of water molecule in Mohr' salt $= 6$.

Formula for potash alum is

$K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$.

$\therefore$ Number of water molecules in potash alum is 12.

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∴ Ratio of water molecules in Mohr's salt and potash alum is

$$\frac{6}{24}=\frac{1}{4}=2.5\times10^{-1}$$

04 Match List I with List II.

	List I		List II
A.	Li	I.	Photoelectric cell
B.	Na	II.	Absorbent of CO_2
C.	K	III.	Coolant in fast breeder nuclear reactor
D.	Cs	IV.	Treatment of cancer
		V.	Bearings for motor engines

Choose the correct answer from the options given below.

[2021, 27 July Shift-II]

	A	B	C	D
(a)	V	I	II	IV
(b)	V	II	IV	I
(c)	IV	III	I	II
(d)	V	III	II	I

Ans. ***(d)***

(A) Li makes alloy with lead which is used to make metal bearings for motor engines.

(B) Liquid Na is used as coolant in fast breeder nuclear reactor.

(C) K is used as absorbent of CO_2.

(D) Cs is used in making photoelectric cell.

Hence, the correct match is

A → V; B → III; C → II; D → I

05 Match List-I with List-II.

	List-I		List-II
A.	NaOH	I.	Acidic
B.	$Be(OH)_2$	II.	Basic
C.	$Ca(OH)_2$	III.	Amphoteric
D.	$B(OH)_3$		
E.	$Al(OH)_3$		

Choose the most appropriate answer from the options given below

[2021, 27 July Shift-I]

	A	B	C	D	E
(a)	II	II	III	II	III
(b)	II	III	II	I	III
(c)	II	II	III	I	III
(d)	II	I	II	III	III

Ans. ***(b)***

s-block elements form metal hydroxide that are basic in nature except $Be(OH)_2$.

Be and Al are diagonally related, their hydroxide are amphoteric in nature.

Boron (non-metal) forms oxide [$B(OH)_3$] which is acidic in nature.

A. NaOH → Basic

B. $Be(OH)_2$ → Amphoteric

C. $Ca(OH)_2$ → Basic

D. $B(OH)_3$ → Acidic

E. $Al(OH)_3$ → Amphoteric

Hence, correct match is

A → II, B → III, C → II, D → I, E → III.

06 Given below are two statements.

One is labelled as Asseriton A and the other labelled as Reason R.

Assertion A Lithium halides are some what covalent in nature.

Reason R Lithium possess high polarisation capability.

According the above statements, choose the most appropriate answer from the options given below **[2021, 27 July Shift-I]**

(a) A is true but R is false

(b) A is false but R is true

(c) Both A and R are true but R is not the correct explanation of A

(d) Both A and R are true and R is the correct explanation of A

Ans. ***(d)***

Both Assertion and Reason are true and Reason is the correct explanation of Assertion.

Lithium ion due to its smaller size than other alkali metal cation has very high polarisation power and least electropositive character. Which results into increase in covalent nature in the molecule [Fajan's rule].

07 Match List I with List II.

	List I (Elements)		List II (Properties)
(A)	Li	I.	Poor water solubility of I^- salt
(B)	Na	II.	Most abundant element in cell fluid
(C)	K	III.	Bicarbonate salt used in fire extinguisher
(D)	Cs	IV.	Carbonate salt decomposes easily on heating

Choose the correct answer from the options given below.

[2021, 25 July Shift-II]

	A	B	C	D
(a)	IV	III	II	I
(b)	I	III	II	IV
(c)	IV	II	III	I
(d)	I	II	III	IV

Ans. ***(a)***

(A) Li_2CO_3 decomposes easily on heating due to high covalent character caused by small size Li^+ cation.

(B) $NaHCO_3$ is used in fire extinguisher. $NaHCO_3$ reacts with acid to produce carbon dioxide.

(C) K is most abundant element in cell fluid.

(D) CsI salt has poor water solubility due to its low hydration energy. As hydration energy is inversely proportional to the size of ion. Both Cs and I are larger in size.

Hence, correct match is

A → IV, B → III, C → II, D → I.

08 A *s*-block element (*M*) reacts with oxygen to form an oxide of the formula MO_2. The oxide is pale yellow in colour and paramagnetic. The element (*M*) is

[2021, 20 July Shift-I]

(a) Mg (b) Na (c) Ca (d) K

Ans. ***(d)***

The element (*M*) is potassium (K). It reacts with O_2 to form KO_2, which is paramagnetic in nature. All other elements form oxides or peroxides which are diamagnetic in nature.

Chemical reaction is as follows

$$\underset{\text{(Paramagnetic)}}{K + O_2\,(\text{excess}) \longrightarrow} \underset{\text{Superoxide}}{KO_2}$$

whereas,

(a) $2Mg + O_2 \longrightarrow 2MgO$ (Diamagnetic)

(b) $2Na + O_2 \longrightarrow Na_2O$ (Diamagnetic)

$2Na + O_2\,(\text{excess}) \longrightarrow Na_2O_2$ (Diamagnetic)

(c) $2Ca + O_2 \longrightarrow 2CaO$ (Diamagnetic)

$Ca + O_2 \longrightarrow CaO_2$ (Diamagnetic)

09 The ionic radius of Na^+ ions is 1.02 Å. The ionic radii (in Å) of Mg^{2+} and Al^{3+}, respectively, are

[2021, 18 March Shift-I]

(a) 1.05 and 0.99 (b) 0.72 and 0.54

(c) 0.85 and 0.99 (d) 0.68 and 0.72

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Ans. ***(b)***

For iso-electronic system, radius is inversely proportional to the $Z_{eff.}$. The effective nuclear charge (Z_{eff}) is net positive charge, experienced by an electron in a multi-electron atom.

$$\underbrace{Na^+ \quad Mg^{2+} \quad Al^{3+}}$$
$$Z=11 \quad Z=12 \quad Z=13$$
(10 electrons in each)

(Z = atomic number)

We know that, more is the positive charge on an ion, smaller will be its ionic radii. Whereas more is the negative charge on an ion more will be its ionic radii.

So, order of ionic size

$$Na^+ > Mg^{2+} > Al^{3+}$$

Ionic radii of Na^+ (1.02 Å) > Mg^{2+} (0.72 Å) > Al^{3+} (0.54 Å).

10 The correct order of conductivity of ions in water is

[2021, 17 March Shift-I]

(a) $Na^+ > K^+ > Rb^+ > Cs^+$
(b) $Cs^+ > Rb^+ > K^+ > Na^+$
(c) $K^+ > Na^+ > Cs^+ > Rb^+$
(d) $Rb^+ > Na^+ > K^+ > Li^+$

Ans. ***(b)***

Correct order of conductivity of ions in water is

$$Cs^+ > Rb^+ > K^+ > Na^+$$

$Cs^+(aq)$ has lower hydrated radius so its electrical conductivity is higher.

Extent of hydration depends on charge density on the ion.

As the size of gaseous ion decreases, it get more hydrated in water and hence, the size of aqueous ion increases. When this bulky ion move in solution, it experience greater resistance and hence lower conductivity.

Size of gaseous ion :

$$Cs^+ > Rb^+ > K^+ > Na^+$$

Size of aqueous ion :

$$Cs^+ < Rb^+ < K^+ < Na^+$$

Conductivity:

$$Cs^+ > Rb^+ > K^+ > Na^+$$

11 Match List-I with List-II

	List-I		List-II
A.	Sodium carbonate	(i)	Deacon
B.	Titanium	(ii)	Castner-Kellner
C.	Chlorine	(iii)	van-Arkel
D.	Sodium hydroxide	(iv)	Solvay

Choose the correct answer form the options given below.

[2021, 26 Feb Shift-II]

	A	B	C	D
(a)	(iv)	(iii)	(i)	(ii)
(b)	(i)	(iii)	(iv)	(ii)
(c)	(iv)	(i)	(ii)	(iii)
(d)	(iii)	(ii)	(i)	(iv)

Ans. ***(a)***

(A) Sodium carbonate is manufactured by Solvay process ⇒ (iv) of List-II.

Solvay process's reactions are as follows

In Solvay's process, first ammonia (NH_3) reacts with CO_2 and H_2O to give ammonium bicarbonate (NH_4HCO_3).

This bicarbonate react with NaCl to give sodium bicarbonate ($NaHCO_3$) along with ammonium chloride (NH_4Cl).

At last, $NaHCO_3$ is heated to form sodium carbonate as major product.

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$
$$NH_4HCO_3 + \underset{\text{(Brine)}}{NaCl} \longrightarrow NaHCO_3\downarrow + NH_4Cl$$
$$2NaHCO_3 \xrightarrow{\Delta} \underset{\text{Sodium carbonate}}{\boxed{Na_2CO_3}} + CO_2 + H_2O$$

12 Match List-I with List-II.

	List-I (Salt)		List-II (Flame colour wavelength)
A.	LiCl	1.	455.5 nm
B.	NaCl	2.	670.8 nm
C.	RbCl	3.	780.0 nm
D.	CsCl	4.	589.2 nm

Choose the correct answer from the options given below.

[2021, 24 Feb Shift-II]

	A	B	C	D		A	B	C	D
(a)	4	2	3	1	(b)	2	1	4	3
(c)	1	4	2	3	(d)	2	4	3	1

Ans. ***(d)***

Alkali metal	Colour (Flame)	λ (nm)
Li	Crimson red	670.8
Na	Yellow	589.2
Rb	Red, violet	780.0
Cs	Blue	455.5

Alkali metals have very low value of ionisation energy as compared to other metals. So, alkali metals easily get excited and impart colour to flame.

Hence, Rb is most excited and having high value of wavelength in all alkali metals.

13 Number of amphoteric compounds among the following is ..... .

[2021, 24 Feb Shift-I]

(a) BeO (b) BaO
(c) $Be(OH)_2$ (d) $Sr(OH)_2$

Ans. ***(Two)***

An amphoteric compound is a molecule or ion that can react with both as an acid or as a base.

BeO = Amphoteric
BaO = Basic
$Be(OH)_2$ = Amphoteric
$Sr(OH)_2$ = Basic

Both beryllium compound BeO and $Be(OH)_2$ are amphoteric in nature while compound BaO and $Sr(OH)_2$ are basic in nature, they form alkaline solution in H_2O.

14 The metal mainly used in devising photoelectric cells is

[2020, 2 Sep Shift-I]

(a) Na (b) Li
(c) Cs (d) Rb

Ans. ***(c)***

The expression of kinetic energy (KE) of photoelectrons is : $KE = E - E_0$

where, E = Energy of incident light

E_0 = Threshold energy of the metal used in photoelectric cells

A metal with lower ionisation energy (IE) will have lower value of E_0, also which will increase the value of KE of photoelectrons.

Group-1 metals have lower IE, values and we know the order of IE, of group-I metals will be

IE_1 : Li > Na > K > Rb > Cs

So, the order is E_0 : Li > Na > K > Rb > Cs

KE : Li < Na < K < Rb < Cs

That is why, Cs metal is the best choice in devising photoelectric cells.

15 On combustion of Li, Na and K in excess of air, the major oxides formed, respectively, are

[2020, 4 Sep Shift-I]

(a) Li_2O, Na_2O and K_2O_2
(b) Li_2O, Na_2O_2 and K_2O
(c) Li_2O, Na_2O_2 and KO_2
(d) Li_2O_2, Na_2O_2 and K_2O_2

Ans. ***(c)***

On combustion of Li, Na and K in excess of air, the major oxides formed respectively are Li_2O, Na_2O_2 and KO_2.

Reactions are as follows:

$$Li + \underset{\text{Excess}}{O_2} \longrightarrow \underset{\text{Oxide}}{Li_2O}$$

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$$Na + \underset{\text{Excess}}{O_2} \longrightarrow \underset{\text{Peroxide}}{Na_2O_2}$$

$$K + \underset{\text{Excess}}{O_2} \longrightarrow \underset{\text{Super oxide}}{KO_2}$$

16 Reaction of an inorganic sulphite *X* with dilute H_2SO_4 generates compound *Y*. Reaction of *Y* with NaOH gives *X*. Further, the reaction of *X* with *Y* and water affords compound *Z*. *Y* and *Z* respectively, are **[2020, 6 Sep Shift-II]**

(a) SO_2 and Na_2SO_3
(b) SO_3 and $NaHSO_3$
(c) SO_2 and $NaHSO_3$
(d) S and Na_2SO_3

Ans. ***(c)***

$$\underset{(X)}{Na_2SO_3} \xrightarrow{\text{Dil.}H_2SO_4} \underset{(Y)}{SO_2} \xrightarrow{NaOH} \underset{(X)}{Na_2SO_3}$$

$$\xrightarrow{SO_2 + H_2O} \underset{(Z)}{NaHSO_3}$$

Here, *X*, *Y*, *Z* are

$X = Na_2SO_3$, $Y = SO_2$, $Z = NaHSO_3$

Na_2SO_3 react with dil.H_2SO_4 form sulphur dioxide (SO_2) gas. SO_2 on reaction with NaOH again form Na_2SO_3. By the reaction of SO_2 and H_2O, Na_2SO_3 form $NaHSO_3$.

Here, *X*, *Y*, *Z* are Na_2SO_3, SO_2, $NaHSO_3$ respectively.

17 Among the statements (A)-(D), the correct ones are **[2020, 9 Jan Shift-II]**

(A) lithium has the highest hydration enthalpy among alkali metals.
(B) lithium chloride is insoluble in pyridine.
(C) lithium cannot form ethynide upon its reaction with ethyne.
(D) Both lithium and magnesium react slowly with H_2O.

(a) (A) and (D) only
(b) (B) and (C) only
(c) (A), (C) and (D) only
(d) (A), (B) and (D) only

Ans. ***(c)***

Statement (A), (C) and (D) are correct whereas statement (B) is incorrect. It's corrected form is that lithium chloride is soluble in pyridine.

18 The correct order of hydration enthalpies of alkali metal ions is **[2019, 8 April Shift-I]**

(a) $Li^+ > Na^+ > K^+ > Cs^+ > Rb^+$
(b) $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$
(c) $Na^+ > Li^+ > K^+ > Cs^+ > Rb^+$
(d) $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Ans. ***(d)***

Key Idea The amount of energy released when one mole of gaseous ions combine with water to form hydrated ions is called hydration enthalpy.

The correct order of hydration enthalpies of alkali metal ions is

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

Li^+ possesses the maximum degree of hydration due to its small size. As a consequence of hydration enthalpy, their mobility also get affected. Cs^+ has highest and Li^+ has lowest mobility in aqueous solution.

19 The incorrect statement is **[2019, 12 April Shift-II]**

(a) lithium is the strongest reducing agent among the alkali metals.
(b) lithium is least reactive with water among the alkali metals.
(c) $LiNO_3$ decomposes on heating to give $LiNO_2$ and O_2.
(d) LiCl crystallise from aqueous solution as $LiCl \cdot 2H_2O$.

Ans. ***(c)***

Statement (c) is incorrect. $LiNO_3$ (Lithium nitrate) on heating gives a mixture of Li_2O, NO_2 and O_2.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 \uparrow + O_2 \uparrow$$

Among the alkali metals, lithium is the strongest reducing agent.

20 Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of **[2019, 10 Jan Shift-II]**

(a) sodium ammonia complex
(b) sodium ion-ammonia complex
(c) sodamide
(d) ammoniated electrons

Ans. ***(d)***

Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of ammoniated electrons. The reaction is represented as follows :

$$Na(s) + (x+y)NH_3(l) \longrightarrow \underset{\substack{\text{[Ammoniated Na}^+\\ \text{or expanded Na]}}}{[Na(NH)_x]^+} + \underset{\substack{\text{[Ammoniated}\\ \text{electrons]}}}{[e_{(NH_3)_y}]}$$

Ammoniated (solvated) electrons show electronic transition in visible region and the solution becomes deep blue coloured.

This deep blue solution also shows the following properties due to the presence of ammoniated electrons.

(i) It is strongly reducing in nature.
(ii) It is paramagnetic.
(iii) It is a good conductor of electricity.

21 NaH is an example of

(a) metallic hydride
(b) electron-rich hydride
(c) saline hydride
(d) molecular hydride **[2019, 11 Jan Shift-I]**

Ans. ***(c)***

$\overset{\oplus}{Na}\overset{\ominus}{H}$ is an example of ionic or saline hydride. These hydrides are formed when hydrogen combines with metals having less electronegativity and more electropositive character with respect to hydrogen. Except Be and Mg, all *s*-block metals form saline hydrides.

Hydrides of *p*-block elements are covalent in nature, *viz*, electron deficient hydrides (by group-13 elements), electron-precise hydrides (by group-14 elements), and electron-rich hydrides (by group 15-17 elements). Hydrides of *d*, *f*-block metals are called interstitial or metallic hydrides.

22 The correct statement(s) among I to III with respect to potassium ions that are abundant within the cell fluids is/are

I. They activate many enzymes.
II. They participate in the oxidation of glucose to produce ATP.
III. Along with sodium ions, they are responsible for the transmission of nerve signals.

(a) I, and III only
(b) I, II and III
(c) I and II only
(d) III only **[2019, 12 Jan Shift-II]**

Ans. ***(b)***

All the statements are correct. K^+ being metallic unipositive ions work as enzyme activators.

These also participate in many reactions of glycolysis and Kreb's cycle to produce ATP from glucose.

Being unipositive these are also equally responsible for nerve signal transmission along with Na^+. (Na^+ ion-pump theory)

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23 Sodium salt of an organic acid '*X*' produces effervescence with conc. H_2SO_4. '*X*' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. '*X*' is **[JEE Main 2017]**

(a) C_6H_5COONa (b) $HCOONa$
(c) CH_3COONa (d) $Na_2C_2O_4$

Ans. ***(d)***

The reaction takes place as follows

$$\underset{(X)}{Na_2C_2O_4} + \underset{(conc.)}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O + \underset{\text{Effervescence}}{CO\uparrow + CO_2\uparrow}$$

$$\underset{(X)}{Na_2C_2O_4} + CaCl_2 \longrightarrow \underset{\text{White ppt.}}{CaC_2O_4} + 2NaCl$$

$$5\underset{\text{Purple}}{CaC_2O_4} + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 5CaSO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Colourless

Hence, *X* is $Na_2C_2O_4$.

24 The main oxides formed on combustion of Li, Na and K in excess of air respectively are **[JEE Main 2016]**

(a) LiO_2, Na_2O_2 and K_2O
(b) Li_2O_2, Na_2O_2 and KO_2
(c) Li_2O, Na_2O_2 and KO_2
(d) Li_2O , Na_2O and KO_2

Ans. ***(c)***

$$\underset{\text{(Excess)}}{2Li + \frac{1}{2}O_2(g)} \longrightarrow Li_2O$$

$$\underset{\text{(Excess)}}{2Na + O_2(g)} \longrightarrow Na_2O_2$$

$$\underset{\text{(Excess)}}{K + O_2(g)} \longrightarrow KO_2$$

25 The products obtained on heating $LiNO_3$ will be **[AIEEE 2011]**

(a) $LiNO_2 + O_2$ (b) $Li_2O + NO_2 + O_2$
(c) $Li_3N + O_2$ (d) $Li_2O + OH + O_2$

Ans. ***(b)***

$LiNO_3$ behave differently from other alkali metal nitrates.

Lithium nitrates decompose on heating producing NO_2. Whereas other alkali nitrates like $NaNO_3$ produces nitrite and oxygen on decomposition.

$$2Li\ NO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 + \frac{1}{2}O_2$$

$$NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$$

26 What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water? **[AIEEE 2011]**

(a) Oxidation number of sodium decreases
(b) Oxide ion accepts a shared pair of electrons
(c) Oxide ion donates a pair of electrons
(d) Oxidation number of oxygen increases

Ans. ***(c)***

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Oxidation number of Na and Oxygen $+1\ -2 \quad -2\ +1\ +2$

No change in oxidation number, so (a) and (d) are not true.

(b) is also not true.

Oxide ion donates a pair of electrons, thus changes to OH^-.

27 KO_2 is used in space and submarines because it

(a) absorbs CO_2 and increases O_2 concentration
(b) absorbs moisture
(c) absorbs CO_2
(d) produces ozone **[AIEEE 2002]**

Ans. ***(a)***

$$4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$$

TOPIC 2
Group 2 Elements (Alkaline Metals)

28 The major component/ingredient of Portland cement is **[2021, 31 Aug Shift-I]**

(a) tricalcium aluminate
(b) tricalcium silicate
(c) dicalcium aluminate
(d) dicalcium silicate

Ans. ***(b)***

The major component of Portland cement is tricalcium silicate (51%, $3CaO{\cdot}SiO_2$). Hence, correct option is (b).

29 The number of water molecules in gypsum, dead burnt plaster and plaster of Paris, respectively are **[2021, 27 Aug Shift-I]**

(a) 2, 0 and 1
(b) 0.5, 0 and 2
(c) 5, 0 and 0.5
(d) 2, 0 and 0.5

Ans. ***(d)***

The chemical formula of gypsum – $CaSO_4{\cdot}2H_2O$, dead burnt plaster – $CaSO_4$ and plaster of Paris – $CaSO_4{\cdot}\frac{1}{2}H_2O$.

So, number of water molecules in gypsum, dead burnt plaster and plaster of Paris are 2, 0 and 0.5 respectively.

30 Given below are two statements : One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Barium carbonate is insoluble in water and is highly stable.

Reason (R) The thermal stability of the carbonates increases with increasing cationic size. **[2021, 26 Aug Shift-II]**

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) (A) is true but (R) is false.
(c) Both (A) and (R) are true and (R) is not the true explanation of (A).
(d) (A) is false but (R) is true.

Ans. ***(a)***

Both Assertion and Reason are true and Reason is the correct explanation of Assertion.

Stability of group-2 metal carbonates increases as we move down the group because large cations are stabilised by large anion and *vice-versa*. Carbonates being a large anion is stabilised by larger cations.

$$\underset{\text{Stability increases}}{\xrightarrow{BeCO_3\ MgCO_3\ CaCO_3\ SrCO_3\ BaCO_3}}$$

Solubility in water decreases as we move down the group because of decrease in hydration energy of cations.

31 What are the products formed in sequence when excess of CO_2 is passed in slaked lime? **[2021, 26 Aug Shift-I]**

(a) $Ca(HCO_3)_2$, $CaCO_3$
(b) $CaCO_3$, $Ca(HCO_3)_2$
(c) CaO, $Ca(HCO_3)_2$
(d) CaO, $CaCO_3$

Ans. ***(b)***

When excess of CO_2 passes through slaked lime [$Ca(OH)_2$], the calcium carbonate ($CaCO_3$) and calcium hydrogen carbonate $Ca(HCO_3)_2$ will be formed as follows

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$$\underset{\text{Slaked lime}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{Calcium carbonate}}{CaCO_3\downarrow} + \underset{\text{(Milky)}}{H_2O}$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{\text{Calcium hydrogen carbonate}}{Ca(HCO_3)_2}$$

32 The conversion of hydroxyapatite occurs due to presence of F^- ions in water. The correct formula of hydroxyapatite is

[2021, 26 Aug Shift-I]

(a) $[3Ca_3(PO_4)_2\,Ca(OH)_2]$
(b) $[3Ca(OH)_2\,CaF_2]$
(c) $[Ca_3(PO_4)_2\,CaF_2]$
(d) $[3Ca_3(PO_4)_2\,CaF_2]$

Ans. ***(a)***

The correct formula for hydroxyapatite is $3[Ca_3(PO_4)_2\,Ca(OH)_2]$. The presence of F^- ions on enamel make the enamel much harder as hydroxyapatite $[3Ca_3(PO_4)_2\,Ca(OH)_2]$ converts into fluoroapatite $[3Ca_3(PO_4)_2\,CaF_2]$.

33 Match List I with List II.

	List-I (Elements)		List-II (Properties)
A.	Ba	(i)	Organic solvent soluble compounds
B.	Ca	(ii)	Outer electronic configuration $6s^2$
C.	Li	(iii)	Oxalate insoluble in water
D.	Na	(iv)	Formation of very strong monoacidic base

Choose the correct answer from the options given below

[2021, 22 July Shift-II]

	A	B	C	D
(a)	(ii)	(iii)	(i)	(iv)
(b)	(iv)	(i)	(ii)	(iii)
(c)	(iii)	(ii)	(iv)	(i)
(d)	(i)	(iv)	(ii)	(iii)

Ans. ***(a)***

Outer electronic configuration of given elements are

$Li \rightarrow 2s^1$; $Na \rightarrow 3s^1$
$Ca \rightarrow 4s^2$; $Ba \rightarrow 6s^2$

(A) $Ba \rightarrow$ Outer electronic configuration $\rightarrow 6s^2$. i.e. (ii).
(B) $Ca \rightarrow$ Calcium oxalate $(CaC_2O_4) \rightarrow$ insoluble in water i.e. (iii).
(C) $Li \rightarrow$ Being small in size, the compounds of lithium are covalent in nature, so its compounds are soluble in organic solvent.
e.g. LiCl is soluble in pyridine i.e (i).
(D) $Na \rightarrow$ NaOH, strong monoacidic base i.e. (iv).

The correct match is :
(A)-(ii), (B)-(iii), (C)-(i) and D-(iv).

34 Match List-I with List-II.

List-I		List-II	
(A)	$Ca(OCl)_2$	(i)	Antacid
(B)	$CaSO_4\cdot\frac{1}{2}H_2O$	(ii)	Cement
(C)	CaO	(iii)	Bleach
(D)	$CaCO_3$	(iv)	Plaster of Paris

Choose the most appropriate answer from the options given below.

[2021, 18 March Shift-I]

	A	B	C	D
(a)	(i)	(iv)	(iii)	(ii)
(b)	(iii)	(ii)	(iv)	(i)
(c)	(iii)	(iv)	(ii)	(i)
(d)	(iii)	(ii)	(i)	(iv)

Ans. ***(c)***

A. $Ca(OCl)_2 \rightarrow$ Bleaching powder
B. $CaSO_4\cdot 1/2H_2O \rightarrow$ Plaster of Paris
C. $CaO \rightarrow$ is major component of cement
D. $CaCO_3 \rightarrow$ used as an antacid
Correct match is (A-iii), (B-iv), (C-ii), (D-i).

35 One of the by-products formed during the recovery of NH_3 from solvay process is

[2021, 17 March Shift-II]

(a) $Ca(OH)_2$ (b) $NaHCO_3$
(c) $CaCl_2$ (d) NH_4Cl

Ans. ***(c)***

$CaCl_2$ is one of the by-products formed during the recovery of NH_3 from Solvay process.

Ammonia required for the process can be prepared by heating ammonium chloride with calcium hydroxide.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + H_2O$$

Hence, the only by-product of the reaction is calcium chloride.

36 Given below are two statements.

Statement I Both $CaCl_2\cdot 6H_2O$ and $MgCl_2\cdot 8H_2O$ undergo dehydration on heating.

Statement II BeO is amphoteric, whereas the oxides of other elements in the same group are acidic.

In the light of the above statements, choose the correct answer from the options given below. **[2021, 16 March Shift-I]**

(a) Statement I is false but statement II is true
(b) Both statement I and statement II are false
(c) Both statement I and statement II are true
(d) Statement I is true but statement II is false

Ans. ***(b)***

The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr, Ba is possible but hydrated halides of Be and Mg on heating suffer hydrolysis due to their small size or high charge density.

$$CaCl_2\cdot 6H_2O \xrightarrow{\Delta} \underset{\text{Anhydrous}}{CaCl_2} + 6H_2O$$

$$MgCl_2\cdot 8H_2O \xrightarrow{\Delta} MgO + 7H_2O + 2HCl$$

$MgCl_2$ can be made anhydrous by heating in presence of dry HCl.

$$MgCl_2\cdot 6H_2O \xrightarrow[\text{Dry HCl}(g)]{\Delta\ (\text{Calcination})} MgCl_2 + 8H_2O$$

Hence, on heating $CaCl_2\cdot 6H_2O$ undergoes dehydration but $MgCl_2\cdot 8H_2O$ does not.

Metal oxides are generally basic. In alkaline earth metal BeO is amphoteric and shows anomalous behaviour while other oxides are basic.

So, both statement I and statement II are false.

37 The correct set from the following in which both pairs are in correct order of melting point is

[2021, 24 Feb Shift-II]

(a) LiF > LiCl, MgO > NaCl
(b) LiCl > LiF, NaCl > MgO
(c) LiF > LiCl, NaCl > MgO
(d) LiCl > LiF, MgO > NaCl

Ans. ***(a)***

Correct option is (a) i.e. LiF > LiCl; MgO > NaCl. Melting point is directly proportional to lattice energy. Lattice energy is the energy required to separate a mole of an ionic solid into gaseous ions.

It depends upon charge of ions and size of ions.

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$$M.P \propto L.E \propto \frac{Charge}{Size}$$

$Li \rightarrow +1$ $\quad$ $Li \rightarrow +1$

$F = -1$ $\quad$ $Cl \rightarrow -1$

Both LiF and LiCl having same charge, so melting point will depend on size.

Larger the size of anion, lesser the lattice energy and hence, melting point order is LiF > LiCl.

Similarly, MgO $\quad$ NaCl

$Mg \rightarrow 2+$ $\quad$ $Na \rightarrow 1+$

$O \rightarrow 2-$ $\quad$ $Cl \rightarrow 1-$

MgO having +2 charge which is greater than NaCl (+1) charge. So, greater the charge on the ions greater will be lattice energy and hence, melting point order is MgO > NaCl.

38 Two elements *A* and *B* have similar chemical properties. They don't form solid hydrogencarbonates, but react with nitrogen to form nitrides. *A* and *B*, respectively, are **[2020, 2 Sep Shift-II]**

(a) Na and Rb (b) Na and Ca
(c) Cs and Ba (d) Li and Mg

Ans. ***(d)***

Group-2 metals (Be, Mg, Ca, Sr, Ba) form nitrides ($\overset{II}{M}_3N_2$) and their hydrogen- or bicarbonates [$\overset{II}{M}(HCO_3)_2$] are known only in solution phase (in situ).

$$M + N_2 \xrightarrow{\Delta} \overset{II}{M}_3N_2$$

$$\overset{II}{M}CO_3(s) + CO_2(g) + H_2O(l) \xrightarrow{25\,^\circ C} \overset{II}{M}(HCO_3)_2(aq)$$

The above two properties are not given by group-I metals (Li, Na, K, Rb Cs) except Li. Li resembles with group-II metals in comparison of their chemical properties.

Specifically, Li (*A*) and Mg (*B*) have similar chemical properties as they show "diagonal relationship" in the periodic table.

2nd period : Li Be B C N O F

3rd period : Na Mg Al Si P S Cl

39 Among the statements (I-IV), the correct ones are :

(I) Be has smaller atomic radius compared to Mg.
(II) Be has higher ionisation enthalpy than Al.
(III) Charge/radius ratio of Be is greater than that of Al.
(IV) Both Be and Al form mainly covalent compounds. **[2020, 3 Sep Shift-II]**

(a) (II), (III) and (IV) (b) (I), (II) and (IV)
(c) (I), (III) and (IV) (d) (I), (II) and (III)

Ans. ***(b)***

Statements (I), (II) and (IV) are correct whereas statement (III) is incorrect.

Corrected statement is

(Charge/Radius) of Be and Al is same because of diagonal relationship.

40 An alkaline earth metal '*M*' readily forms water soluble sulphate and water insoluble hydroxide. Its oxide *MO* is very stable to heat and does not have rock-salt structure. *M* is **[2020, 4 Sep Shift-II]**

(a) Sr (b) Ca
(c) Be (d) Mg

Ans. ***(c)***

Solubility of $BeSO_4$ is highest among the given options and order is as follows :

$$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$$

$BeSO_4$ is water soluble sulphate and $Be(OH)_2$ is insoluble.

BeO is stable to heat and does not form rock salt like structure.

41 Match the following compounds (Column -I) with their uses (Columns -II).

	Column -I		Column - II
(I)	$Ca(OH)_2$	(A)	Casts of statues
(II)	NaCl	(B)	White wash
(III)	$CaSO_4 \cdot \frac{1}{2}H_2O$	(C)	Antacid
(IV)	$CaCO_3$	(D)	Washing soda preparation

[2020, 6 Sep Shift-II]

(a) (I)-(D), (II)-(A), (III)-(C), (IV)-(B)
(b) (I)-(B), (II)-(D), (III)-(A), (IV)-(C)
(c) (I)-(B), (II)-(C), (III)-(D), (IV)-(A)
(d) (I)-(C), (II)-(D), (III)-(B), (IV)-(A)

Ans. ***(b)***

Correct match is I → (B), II → (D), III → (A), IV → (C)

(I) $Ca(OH)_2$ used in white wash.
(II) NaCl is used in the preparation of washing soda.

$$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + NaHCO_3(s)$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

(III) $CaSO_4 \cdot \frac{1}{2}H_2O$ (plaster of Paris) is used for making casts of statues.

(IV) $CaCO_3$ is used as an antacid.

42 Among the sulphates of alkaline earth metals, the solubilities of $BeSO_4$ and $MgSO_4$ in water, respectively, are **[2020, 6 Sep Shift-I]**

(a) poor and poor (b) high and poor
(c) high and high (d) poor and high

Ans. ***(c)***

Hydration enthalpies of $BeSO_4$ and $MgSO_4$ are quite high because of small size of Mg^{2+} and Be^{2+} ions. These hydration enthalpy values are higher than their corresponding lattice enthalpies and therefore, $BaSO_4$ and $MgSO_4$ are highly soluble in water.

Hence, the correct option is (c).

43 In the following reactions, products (*A*) and (*B*), respectively, are

$NaOH + Cl_2 \rightarrow (A) +$ side products (hot and conc.)

$Ca(OH)_2 + Cl_2 \rightarrow (B) +$ side products (dry) **[2020, 7 Jan Shift-II]**

(a) $NaClO_3$ and $Ca(OCl)_2$
(b) $NaClO_3$ and $Ca(ClO_3)_2$
(c) NaOCl and $Ca(OCl)_2$
(d) NaOCl and $Ca(ClO_3)_2$

Ans. ***(a)***

$$\underset{\text{(Hot and conc.)}}{6NaOH} + 3Cl_2 \longrightarrow \underset{(A)}{NaClO_3} + 5NaCl + 3H_2O$$

$$\underset{\text{(Dry)}}{2Ca(OH)_2} + 2Cl_2 \longrightarrow \underset{(B)}{Ca(OCl)_2} + CaCl_2 + 2H_2O$$

Thus, $A : NaClO_3$; $B : Ca(OCl)_2$

44 When gypsum is heated to 393 K, it forms : **[2020, 8 Jan Shift-I]**

(a) Dead burnt plaster
(b) $CaSO_4 \cdot 0.5H_2O$
(c) $CaSO_4 \cdot 5H_2O$
(d) Anhydrous $CaSO_4$

Ans. ***(b)***

When gypsum is heated to 393 K, it forms, plaster of Paris $CaSO_4 . 0.5H_2O$.

The reaction is as follows :

$$CaSO_4 . 2H_2O \xrightarrow[393\,K]{\Delta} CaSO_4 . 0.5H_2O$$

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45 A metal (*A*) on heating in nitrogen gas gives compound *B*. *B* on treatment with H_2O gives a colourless gas, which when passed through $CuSO_4$ solution gives a dark blue-violet coloured solution. *A* and *B* respectively, are **[2020, 8 Jan Shift-II]**

(a) Na and Na_3N
(b) Mg and Mg_3N_2
(c) Mg and $Mg(NO_3)_2$
(d) Na and $NaNO_3$

Ans. ***(b)***

According to the question,

$A = Mg$ and $B = Mg_3N_2$

Complete reactions are as follows :

$$6Mg + 2N_2 \longrightarrow 2Mg_3N_2$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$Cu^{2+} + 4NH_3 \longrightarrow \underset{\text{(dark blue violet colour)}}{[Cu(NH_3)_4]^{2+}}$$

46 The covalent alkaline earth metal halide (X = Cl, Br, I) is **[2019, 8 April Shift-II]**

(a) SrX_2 (b) CaX_2
(c) MgX_2 (d) BeX_2

Ans. ***(d)***

Key Idea According to Fajan's rule, degree of covalency (ionic potential), $\phi \propto$ polarisation power of the cation $\propto$ charge on the cation

$$\propto \frac{1}{\text{size of the cation}}.$$

Alkaline earth metals contains bipositive (M^{2+}) ions in their compounds. So, here

(i) Charge on cation, i.e. + 2 is constant.
(ii) Halide present (X^-) is also constant.

So, the covalent character depends on the size of alkaline earth metal. As we move down the group, size of metal ion increases.

$Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$

So, Be^{2+} readily forms covalent compounds like BeX_2, because of very high positive charge density over its small size, so that it readily polarises anionic spherical electron cloud.

47 Magnesium powder burns in air to give **[2019, 9 April Shift-I]**

(a) MgO and Mg_3N_2
(b) $Mg(NO_3)_2$ and Mg_3N_2
(c) MgO only
(d) MgO and $Mg(NO_3)_2$

Ans. ***(a)***

Magnesium powder burns in air to give MgO and Mg_3N_2. MgO does not combine with excess oxygen to give any superoxide. Mg reacts with nitrogen to form magnesium nitride (Mg_3N_2).

$$Mg + O_2 \longrightarrow MgO$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

48 The structures of beryllium chloride in the solid state and vapour phase, respectively are **[2019, 9 April Shift-II]**

(a) dimeric and dimeric
(b) chain and chain
(c) dimeric and chain
(d) chain and dimeric

Ans. ***(d)***

The structures of beryllium chloride in the solid state and vapour phase, respectively are dimeric and chain. In vapour phase at above 900°C, $BeCl_2$ is monomeric having a linear structure Cl—Be—Cl. The bonding in $BeCl_2$ is covalent and Be atom accommodates 2 + 2 = 4 electrons in the two *sp*-hybrid orbitals. Below 900°C, beryllium chloride in vapour phase exists as a mixture of monomer $BeCl_2$ and dimer Be_2Cl_4.

49 A hydrated solid *X* on heating initially gives a monohydrated compound *Y*. *Y* upon heating above 373 K leads to an anhydrous white powder *Z*. *X* and *Z*, respectively, are **[2019, 10 April Shift-II]**

(a) baking soda and soda ash
(b) washing soda and soda ash
(c) baking soda and dead burnt plaster
(d) washing soda and dead burnt plaster

Ans. ***(b)***

Baking soda ($NaHCO_3$) is not a hydrated solid. Thus, (*X*) is not baking soda. Thus, option (a) and (c) are incorrect. Dead burnt plaster ($CaSO_4$) is obtained from gypsum *via* the formation of plaster of Paris.

$$\underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O} \xrightarrow[-1/2\,H_2O]{380\text{-}393\ K} \underset{\text{Plaster of Paris}}{CaSO_4 \cdot \frac{1}{2}H_2O} \xrightarrow[-\frac{1}{2}H_2O]{>393K} \underset{\substack{\text{Dead burnt}\\ \text{plaster}\\ \text{(anhydrous)}}}{CaSO_4}$$

Therefore, the reaction takes place as follows :

$$\underset{\substack{\text{Washing soda}\\ (X)}}{Na_2CO_3 \cdot 10H_2O} \xrightarrow[-9H_2O]{<373K} \underset{\substack{\text{Monohydrate}\\ (Y)}}{Na_2CO_3 \cdot H_2O} \xrightarrow[-H_2O]{>373K} \underset{\substack{\text{Anhydrous white powder}\\ \text{(soda ash)}(Z)}}{Na_2CO_3}$$

50 The correct sequence of thermal stability of the following carbonates is **[2019, 12 April Shift-I]**

(a) $BaCO_3 < CaCO_3 < SrCO_3 < MgCO_3$
(b) $MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
(c) $MgCO_3 < SrCO_3 < CaCO_3 < BaCO_3$
(d) $BaCO_3 < SrCO_3 < CaCO_3 < MgCO_3$

Ans. ***(b)***

The correct sequence of thermal stability of carbonates is

$$MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$$

On moving down the group, i.e. from Mg to Ba, atomic radius generally increases. It is due to the addition of shell. As a result, the atomic size increases. CO_3^{2-} is a large anion. Hence, more stabilised by Ba^{2+} (large cation) and less stabilised by Mg^{2+}. Therefore, $BaCO_3$ has highest thermal stability followed by $SrCO_3$, $CaCO_3$ and $MgCO_3$.

51 The alkaline earth metal nitrate that does not crystallise with water molecules, is

(a) $Ca(NO_3)_2$ (b) $Sr(NO_3)_2$
(c) $Ba(NO_3)_2$ (d) $Mg(NO_3)_2$ **[2019, 9 Jan Shift-I]**

Ans. ***(c)***

A saturated aqueous solution of $\overset{\downarrow}{M}(NO_3)_2$ on crystallisation will produce hydrated crystal, $\overset{II}{M}(NO_3)_2 \cdot nH_2O$ only when hydration enthalpy ($\Delta H°_{hyd}$) of M^{2+} ion will be appreciably more negative.

Hydration of an ion depends on its size. Smaller the size of an ion, higher will be its charge density and as a result it will remain more solvated (hydrated) through ion dipole interaction.

Size of group-2 metal ions increases on going down the group. So, their ability to form hydrated crystals follows the order:

$Be^{2+} >> Mg^{2+} >> Ca^{2+} >> Sr^{2+} >> Ba^{2+}$

Thus, $Ba(NO_3)_2$ is slightly or almost insoluble in water.

52 The metal used for making X-ray tube window is **[2019, 10 Jan Shift-I]**

(a) Na (b) Be
(c) Mg (d) Ca

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Ans. *(b)*

Among the four elements given, Na, Be, Mg and Ca, Be has highest IE value because of its smallest size and $2s^2$ valence shell configuration.

So, *X*-ray cannot cause ionisation from the material used, i.e. Be in the tube window, which may cause interference in the study.

53 The amphoteric hydroxide is

(a) $Be(OH)_2$ (b) $Ca(OH)_2$
(c) $Sr(OH)_2$ (d) $Mg(OH)_2$

[2019, 11 Jan Shift-I]

Ans. *(a)*

For group-2 metal hydroxides, basicity increases down the group, as:

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

This is because as the size of metal atom increases, *M*—OH bond length increases or *M*—OH bond become weaker thus readily breaks to release OH^- ions which are responsible for the basicity of these solutions.

But $Be(OH)_2$ shows amphoteric (basic as well as acidic) character as it reacts with acid and alkali both which is shown in the following reactions. $Be(OH)_2$ as a base :

$$Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O$$

$Be(OH)_2$ as an acid :

$$Be(OH)_2 + 2NaOH \longrightarrow Na_2[Be(OH)_4]$$

54 Both lithium and magnesium display several similar properties due to the diagonal relationship; however, the one which is incorrect is **[JEE Main 2017]**

(a) Both form basic carbonates
(b) Both form soluble bicarbonates
(c) Both form nitrides
(d) nitrates of both Li and Mg yield NO_2 and O_2 on heating

Ans. *(a)*

Mg can form basic carbonate while Li can not.

$$5\,Mg^{2+} + 6\,CO_3^{2-} + 7H_2O \longrightarrow 4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O + 2\,HCO_3^-$$

55 Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? **[JEE Main 2015]**

(a) $CaSO_4$ (b) $BeSO_4$
(c) $BaSO_4$ (d) $SrSO_4$

Ans. *(b)*

As we move down the group, size of metal increases. Be has lower size while SO_4^{2-} has bigger size, that's why $BeSO_4$ breaks easily and lattice energy becomes smaller but due to lower size of Be, water molecules are gathered around and hence hydration energy increases.

On the other hand, rest metals i.e. Ca, Ba, Sr have bigger size and that's why lattice energy is greater than hydration energy.

Time Saving Technique In the question of finding hydration energy only check the size of atom. Smaller sized atom has more hydration energy.

Thus, in this question Be is placed upper most in the group has lesser size and not comparable with the size of sulphates. Hence, $BeSO_4$ is the right response.

56 Which of the following on thermal decomposition yields a basic as well as acidic oxide? **[AIEEE 2012]**

(a) $NaNO_3$ (b) $KClO_3$
(c) $CaCO_3$ (d) NH_4NO_3

Ans. *(c)*

(a) $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

(b) $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

(c) $CaCO_3 \xrightarrow{\Delta} \underset{\text{Basic}}{CaO} + \underset{\text{Acidic}}{CO_2}$

(d) $NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$

57 One mole of magnesium nitride on reaction with an excess of water gives **[AIEEE 2004]**

(a) one mole of ammonia
(b) one mole of nitric acid
(c) two moles of ammonia
(d) two moles of nitric acid

Ans. *(c)*

$$\underset{1\,\text{mol}}{Mg_3N_2(s)} + 6H_2O(l) \longrightarrow 3Mg(OH)_2 + \underset{2\,\text{mol}}{2NH_3(g)}$$

58 The solubilities of carbonates decrease down the magnesium group due to a decrease in **[AIEEE 2003]**

(a) lattice energies of solids
(b) hydration energies of cations
(c) inter ionic attraction
(d) entropy of solution formation

Ans. *(b)*

The solubilities of carbonates of the alkaline earth metals decrease down the group mainly due to decreasing hydration ethalpies of the cartions from Be^{2+} to Ba^{2+}.

59 The substance not likely to contain $CaCO_3$, is **[AIEEE 2003]**

(a) a marble statue
(b) calcined gypsum
(c) sea shells (d) dolomite

Ans. *(b)*

Calcined gypsum does not contain $CaCO_3$ as gypsum is $CaSO_4 \cdot 2H_2O$.

i.e., it is sulphate.

60 The substance used in Holmes signals of the ship is a mixture of **[AIEEE 2003]**

(a) $CaC_2 + Ca_3P_2$ (b) $Ca_3(PO_4)_2 + Pb_3O_4$
(c) $H_3PO_4 + CaCl_2$ (d) $NH_3 + HOCl$

Ans. *(a)*

In Holmes signals of the ship, mixture of CaC_2 and Ca_3P_2 is used.

61 A metal *M* forms water soluble MSO_4 and inert $MO \cdot MO$ in aqueous solution forms insoluble $M(OH)_2$, soluble in NaOH. Metal *M* is **[AIEEE 2002]**

(a) Be (b) Mg (c) Ca (d) Sr

Ans. *(a), (b)*

Both $Be(OH)_2$ and $Mg(OH)_2$ being insoluble are obtained from NaOH solution through precipitation.

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17

p-Block Elements

TOPIC 1
Group 13 Elements

01 In which one of the following molecules strongest back donation of an electron pair from halide to boron is expected?

[2021, 27 Aug Shift-I]

(a) BCl_3 (b) BF_3 (c) BBr_3 (d) BI_3

Ans. ***(b)***

Smaller the halide atom, more effective is back donation of an electron pair from halide atom.

So, correct answer is BF_3.

02 Given below are the statements about diborane.

(A) Diborane is prepared by the oxidation of $NaBH_4$ and I_2.

(B) Each boron atom is in sp^2-hybridised state.

(C) Diborane has one bridged 3 centre -2 - electron bond.

(D) Diborane is a planar molecule.

The option with correct statement(s) is **[2021, 22 July Shift-II]**

(a) (C) and (D) only

(b) (A) only

(c) (C) only

(d) (A) and (B) only

Ans. ***(b)***

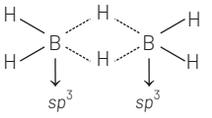
Statement (A) is correct whereas all other options are incorrect. Diborane is prepared by the oxidation of $NaBH_4$ with I_2.

Chemical reaction is as follows:

(A) The oxidation of sodium borohydride with iodine in diglyme gives diborane.

$$I_2 + 2NaBH_4 \xrightarrow{\text{Diglyme}} 2NaI + B_2H_6 + H_2$$

(B)



Hybridisation of boron in B_2H_6 is sp^3.

(C) B_2H_6 has two bridged, 3-centre-2-electron bond.

(D) B_2H_6 is a non-planar molecule.

03 The correct statement about B_2H_6 is **[2021, 25 Feb Shift-I]**

(a) all B—H—B angles are of 120°

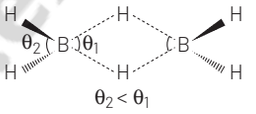
(b) the two B—H—B bonds are not of same length

(c) terminal B—H bonds have less *p*-character when compared to bridging bonds

(d) Its fragment, BH_3, behaves as a Lewis base

Ans. ***(c)***

Statement (c) is correct, whereas all other statements are incorrect.



$\theta_2 < \theta_1$

Correct statements are as follows

- Both B— H —B bridge bond having same bond length.
- B— H —B bond angle is 90°.

BH_3 is electron deficient species and therefore act as Lewis acid.

04 Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce, respectively. **[2019, 8 April Shift-I]**

(a) B_2O_3 and H_3BO_3

(b) B_2O_3 and $[BH_4]^-$

(c) H_3BO_3 and B_2O_3

(d) HBO_2 and H_3BO_3

Ans. ***(a)***

Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce B_2O_3 and H_3BO_3 respectively. Diborane is a colourless, highly toxic gas, having boiling point 180 K. Because of its inflammable nature, it catches fire spontaneously when exposed to air and burns in oxygen releasing an enormous amount of energy as :

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + 1976\ kJ/mol$$

It gets hydrolysed readily to give boric acid.

$$\underset{\text{Borane}}{B_2H_6} + 6H_2O \longrightarrow \underset{\text{Orthoboric acid}}{2H_3BO_3} + \underset{\text{Dihydrogen}}{6H_2}\uparrow$$

05 The correct statements among I to III regarding group 13 element oxides are: **[2019, 9 April Shift-II]**

I. Boron trioxide is acidic.

II. Oxides of aluminium and gallium are amphoteric.

III. Oxides of indium and thallium are basic.

(a) I, II and III (b) I and III only

(c) I and II only (d) II and III only

Ans. ***(a)***

All the given statements are correct. For group 13 elements, the acidic nature of oxides decreases and the basic nature of oxides increases on moving from B to Tl. This is because as we move down the group, the atomic size of elements goes on increasing, whereas the ionisation energy decreases, due to which the strength of metal oxide (MO) bond goes on decreasing.

Thus, boron trioxide or boron oxide is acidic and reacts with basic oxides to give metal borates. Aluminium and gallium oxides are amphoteric while oxides of indium and thallium are basic in nature.

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06 Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to **[2019, 9 Jan Shift-I]**

(a) lattice effect
(b) lanthanoid contraction
(c) inert pair effect
(d) diagonal relationship

Ans. ***(c)***

Due to inert pair effect, group-13 elements (ns^2np^1) show + 3 and + 1 oxidation states in their compounds. Stability order of these oxidation states will be as, + 3 oxidation states

$$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$$

B^{3+} does not exist in free states. All B(III) compounds are covalent.

+ 1 oxidation states

$$B^{+} < Al^{+} < Ga^{+} < In^{+} < Tl^{+}$$

B^{+} does not exist in ionic as well covalent compounds.

07 The electronegativity of aluminium is similar to **[2019, 10 Jan Shift-I]**

(a) lithium (b) carbon
(c) beryllium (d) boron

Ans. ***(c)***

Let, us consider the electronegativity values of the given elements,

	Group-1	Group-2	Group-13	Group-19
Period 2 ⇒	Li (1.0)	Be (1.5)	B (2.0)	C (2.5)
Period 3 ⇒			Al (1.5)	

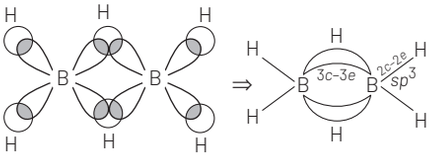
Be and Al show diagonal relationship which is based on their same $\frac{Z^*}{r}$ value (Z^* is effective nuclear charge, r = atomic radius). So, they have similar electronegativity.

08 The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6, respectively, are **[2019, 10 Jan Shift-II]**

(a) 4 and 2 (b) 2 and 4
(c) 2 and 2 (d) 2 and 1

Ans. ***(a)***

The structure of B_2H_6 can be shown as :



In B_2H_6, four 2-centre-2-electron ($2c-2e$) bonds are present in the same plane and two 3-centre-2-electron ($3c-2e$) bonds are present in another plane.

09 The relative stability of +1 oxidation state of group 13 elements follows the order **[2019, 11 Jan Shift-II]**

(a) Al < Ga < Tl < In (b) Al < Ga < In < Tl
(c) Tl < In < Ga < Al (d) Ga < Al < In < Tl

Ans. ***(b)***

The stability order of + 3 and + 1 oxidation states of group 13 elements will be:

$$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} >> Tl^{3+}$$

(order of + 3 oxidation state)

$$B^{+} << Al^{+} < Ga^{+} < In^{+} < Tl^{+}$$

(order of + 1 oxidation state)

The presence of two oxidation states in *p*-block elements is due to the inert pair effect.

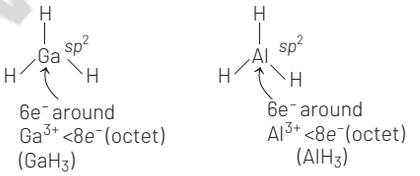
Because of the presence of poor shielding *d* and *f*-orbitals, as we move from Ga to Tl, effective nuclear charge of these elements increases so as to hold the valence ns^2 electrons tightly. It causes difficulty to the ionisation of ns^2-electrons and it remains inert, only np^1-electron ionises to give + 1 oxidation state.

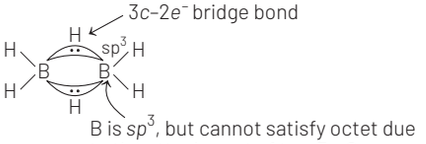
10 The hydride that is not electron deficient is **[2019, 11 Jan Shift-II]**

(a) AlH_3 (b) B_2H_6
(c) SiH_4 (d) GaH_3

Ans. ***(c)***

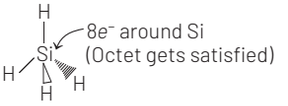
GaH_3, AlH_3 and B_2H_6 are the hydrides of group-13 (ns^2np^1), whereas SiH_4 is an hydride of group 14.





So, B_2H_6, AlH_3 and GaH_3 are electron deficient hydrides.

But, SiH_4 is an electron precise hydride of group-14 (ns^2np^2), i.e. these hydrides can have the required number of electrons to write their conventional Lewis structures.



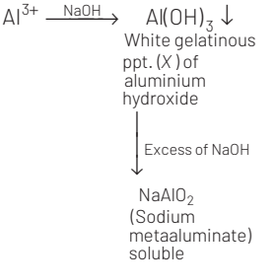
11 When metal '*M*' is treated with NaOH, a white gelatinous precipitate '*X*' is obtained, which is soluble in excess of NaOH. Compound '*X*' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal '*M*' is **[JEE Main 2018]**

(a) Zn (b) Ca (c) Al (d) Fe

Ans. ***(c)***

Among the given metals Al forms white gelatinous ppt. with NaOH. Hence, the probable metal can be Al.

This ppt. is dissolved in excess of NaOH due to the formation of sodium metal Aluminate. Both the reactions are shown below.



Aluminium hydroxide on strong heating gives alumina (Al_2O_3) which is used as an adsorbent in chromatography. This reaction can be seen as :

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

Thus, metal *M* is Al.

Ca, being below sodium in electrochemical reactivity series, cannot displaces Na from its aqueous solution.

Zn reacts with NaOH to form sodium zincate which is a soluble compound.

Fe reacts with sodium hydroxide to form tetrahydroferrate (II) sodium which is again a soluble complex.

12 Boron can't form which one of the following anions? **[AIEEE 2011]**

(a) BF_6^{3-} (b) BH_4^-
(c) $B(OH)_4^-$ (d) BO_2^-

Ans. ***(a)***

B_5 $1s^2$ $2s^2$ $2p^1$

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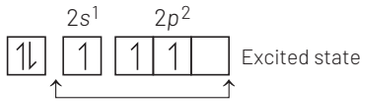


Maximum covalency = 4

Due to absence of 2*d*-orbital, maximum covalency is four. Thus, BF_6^{3-} is not formed.

Therefore, (a) is not formed while BH_4^- ($BH_3 + H^-$), $B(OH)_4^-$, ($B[OH)_3 + OH^-$] and BO_2^- are formed.

13 Which one of the following order represents the correct sequence of the increasing basic nature of the given oxides? **[AIEEE 2011]**

(a) $MgO < K_2O < Al_2O_3 < Na_2O$
(b) $Na_2O < K_2O < MgO < Al_2O_3$
(c) $K_2O < Na_2O < Al_2O_3 < MgO$
(d) $Al_2O_3 < MgO < Na_2O < K_2O$

Ans. ***(d)***

Metallic character decreases on moving along a period in the sequence as Na > Mg > Al and increases down the group.

As metallic character of the element attached to oxygen atom increases, the basic character of oxides increases.

Hence, the increasing correct order of basic nature is $Al_2O_3 < MgO < Na_2O < K_2O$.

14 Among the following, the maximum covalent character is shown by the compound. **[AIEEE 2011]**

(a) $SnCl_2$ (b) $AlCl_3$
(c) $MgCl_2$ (d) $FeCl_2$

Ans. ***(b)***

Greater the charge and smaller the size of the cation, larger the charge density. Thus, greater is the polarization of *M*—Cl bond and hence, maximum covalent character is possessed by the compound.

Among the given species, only $AlCl_3$ possesses maximum covalent charge due to the presence of large charge density on Al^{3+} ion.

15 Which one of the following is the correct statement ? **[AIEEE 2007]**

(a) Boric acid is a protonic acid
(b) Beryllium exhibits coordination number of six
(c) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase
(d) $B_2H_6 \cdot 2NH_3$ is known as 'inorganic benzene'

Ans. ***(c)***

Chlorides of both beryllium and aluminium have bridged structures in solid phase.

16 The type of hybridisation of boron in diborane is **[AIEEE 2007]**

(a) *sp* hybridisation
(b) sp^2 hybridisation
(c) sp^3 hybridisation
(d) sp^3d^2 hybridisation

Ans. ***(c)***

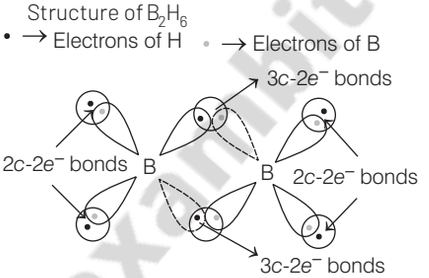
Boron atom in B_2H_6(diborane) is sp^3 hybridised.

17 The structure of diborane (B_2H_6) contains **[AIEEE 2005]**

(a) four $2c - 2e^-$ bonds and four $3c - 2e^-$ bonds
(b) two $2c - 2e^-$ bonds and two $3c - 3e^-$ bonds
(c) two $2c - 2e^-$ bonds and four $3c - 2e^-$ bonds
(d) four $2c - 2e^-$ bonds and two $3c - 2e^-$ bonds

Ans. ***(d)***

Structure of B_2H_6



18 Heating of an aqueous solution of aluminium chloride to dryness will give **[AIEEE 2005]**

(a) $Al(OH)Cl_2$ (b) Al_2O_3
(c) Al_2Cl_6 (d) $AlCl_3$

Ans. ***(b)***

Aqueous solution of $AlCl_3$ is acidic, as it gives HCl on hydrolysis.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

On strongly heating, $Al(OH)_3$ is converted into Al_2O_3.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

19 Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in **[AIEEE 2004]**

(a) exhibiting maximum covalency in compounds
(b) forming polymeric hydrides
(c) forming covalent halides
(d) exhibiting amphoteric nature in their oxides

Ans. ***(a)***

Be ($Z = 4$) has maximum covalency of 4 while Al ($Z = 13$) has maximum covalency of 6.

20 Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives **[AIEEE 2004]**

(a) $Al^{3+} + 3Cl^-$
(b) $[Al[H_2O)_6]^{3+} + 3Cl^-$
(c) $[Al(OH)_6]^{3-} + 3HCl$
(d) $Al_2O_3 + 6HCl$

Ans. ***(b)***

$AlCl_3$ is covalent but in water, it become ionic due to large hydration energy of Al^{3+}.

$$AlCl_3 + 6H_2O \rightleftharpoons [Al(H_2O)_6]^{3+} + 3Cl^-$$

21 Alum is widely used to purify water since

(a) it forms complex with clay particles
(b) it coagulates the mud particles
(c) it exchanges Ca^{2+} and Mg^{2+} ions present in hard water
(d) its sulphate ion is water purifier **[AIEEE 2002]**

Ans. ***(b)***

Mud is colloidal charged solution which on treatment with alum (Al^{3+}) gets neutralised or coagulated.

TOPIC 2
Group 14 Elements

22 Which one of the following compounds of group-14 elements is not known? **[2021, 25 July Shift-I]**

(a) $[GeCl_6]^{2-}$
(b) $[Sn(OH)_6]^{2-}$
(c) $[SiCl_6]^{2-}$
(d) $[SiF_6]^{2-}$

Ans. ***(c)***

In group 14, $[SiCl_6]^{2-}$ does not exist due to steric crowding of surrounding atoms.

The main reasons are:

(i) Six large chloride ions cannot be accommodated around Si^{4+}.
(ii) Interaction between lone pair of chloride ion and Si^{4+} is not very strong.

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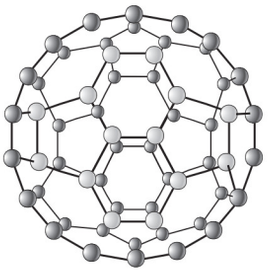
23 The incorrect statement regarding the structure of C_{60} is
[2021, 16 March Shift-II]

(a) the six-membered rings are fused to both six and five-membered rings
(b) each carbon atom forms three sigma bonds
(c) the five-membered rings are fused only to six-membered rings
(d) it contains 12 six-membered rings and 24 five-membered rings

Ans. ***(d)***



C_{60} molecule has a shape like soccer ball and called Buckminster fullerene. It is an allotrope of carbon. It contains twenty-six membered rings and twelve-five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.

All the carbon atoms are equal and they undergo sp^2-hybridisation . Each carbon atom forms three sigma bonds with other three carbon atoms.

So, statement (d) is wrong.

24 Water does not produce CO on reacting with
[2021, 25 Feb Shift-II]

(a) CH_4 (b) C (c) CO_2 (d) C_3H_8

Ans. ***(c)***

Water (steam) can produce CO on reacting with CH_4, C and C_3H_8 as,

$$CH_4 + H_2O \xrightarrow[Ni]{1270\ K} CO + 3H_2$$

$$C + H_2O \xrightarrow{1270\ K} CO + H_2$$

$$C_3H_8 + 3H_2O \xrightarrow[Ni]{1270\ K} 3CO + 7H_2$$

But, water on reaction with CO_2 produces carbonic acid (H_2CO_3), not CO.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

25 '*X*' melts at low temperature and is a bad conductor of electricity in both liquid and solid state. *X* is
[2020, 9 Jan Shift-II]

(a) carbon tetrachloride
(b) silicon carbide
(c) mercury
(d) zinc sulphide

Ans. ***(a)***

'*X*' is carbon tetrachloride. It is a molecular solid. It melts at low temperature and is a bad conductor of electricity in both liquid and solid state.

Other options are explained as follows :

(1)	Silicon carbide	Network (or covalent) solid. Very high melting point. Not electric conductor as solid or liquid.
(2)	Mercury	Metallic solid with an exceptionally low melting point, conduct electricity in both solid and molten forms.
(3)	Zinc sulphide	Ionic crystal. High melting point and conduct electricity in molten state but not as solid.

26 C_{60} an allotrope of carbon contains
[2019, 9 April Shift-I]

(a) 16 hexagons and 16 pentagons
(b) 20 hexagons and 12 pentagons
(c) 12 hexagons and 20 pentagons
(d) 18 hexagons and 14 pentagons

Ans. ***(b)***

C_{60} is aromatic allotrope of carbon containing 12 pentagons and 20 hexagons. It is a fullerene having a shape like soccer ball and called Buckminster fullerene.

27 The amorphous form of silica is
[2019, 9 April Shift-II]

(a) tridymite (b) kieselguhr
(c) cristobalite (d) quartz

Ans. ***(b)***

Silica occurs in nature in several amorphous and crystalline forms. Kieselguhr is the amorphous form of silica. Quartz, tridymite and cristobalite are crystalline forms of silica.

28 The correct order of catenation is
[2019, 10 April Shift-I]

(a) C > Sn > Si ≈ Ge (b) Si > Sn > C > Ge
(c) C > Si > Ge ≈ Sn (d) Ge > Sn > Si > C

Ans. ***(c)***

Catenation property is an unique property of group 14 elements. Down the group 14, catenation power decreases as :

$$C > Si > Ge \approx Sn$$

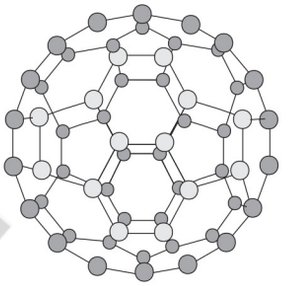
Pb does not show catenation.

29 The number of pentagons in C_{60} and trigons (triangles) in white phosphorus, respectively, are
[2019, 10 April Shift-II]

(a) 20 and 3 (b) 12 and 4
(c) 20 and 4 (d) 12 and 3

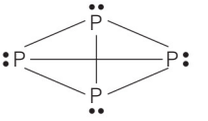
Ans. ***(b)***

In C_{60} (Buckminster fullerene) twenty hexagons and twelve pentagons are present which are interlocked resulting a shape of soccer ball. Every ring in this structure is aromatic.



Structure of C_{60} Buckminster fullerene

Phosphorus has large atomic size and less electronegativity, so it forms single bond instead of $p\pi$-$p\pi$ multiple bond. So, it consists of discrete tetrahedral P_4 molecule as shown below :



∴ Number of trigons (triangles) = 4

30 The basic structural unit of feldspar, zeolites, mica and asbestos is
[2019, 12 April Shift-I]

(a) $(SiO_3)^{2-}$
(b) SiO_2
(c) $(SiO_4)^{4-}$
(d) $-\left(\begin{matrix}R\\|\\Si\\|\\R\end{matrix}-O\right)_n-$ (R = Me)

Ans. ***(c)***

The basic structural unit of feldspar, zeolites, mica and asbestos is $(SiO_4)^{4-}$. These all are silicates. All silicates involve two types of Si—O bonds.

(i) Terminal Si—O bonds in which oxygen is bonded to a silicon and not other atom.
(ii) Bridging Si—O—Si bonds in which oxygen is bonded to two silicon atoms.

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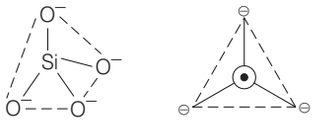

Tetrahedral structure of SiO_4^{2-} anion

In SiO_4^{4-} ion, each Si atom is bonded to four oxygen atoms tetrahedrally.

31 The C —C bond length is maximum in **[2019, 12 April Shift-II]**

(a) graphite (b) C_{70}
(c) C_{60} (d) diamond

Ans. ***(d)***

The C—C bond length is maximum in diamond having value 154 pm. Here, each carbon atom undergoes sp^3-hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. It has a rigid three-dimensional network of carbon atoms.

C—C bond length within the layers of graphite is 141.5 pm. In C_{60}, C— C distances between single and double bonds are 143.5 pm and 138.3 pm respectively.

32 The one that is extensively used as a piezoelectric material is **[2019, 9 Jan Shift-I]**

(a) quartz
(b) tridymite
(c) amorphous silica
(d) mica

Ans. ***(a)***

Piezoelectric materials are those materials that produce an electric current when they are placed under mechanical stress. Crystalline solids can be used as piezoelectric material hence, quartz is a correct answer.

33 Correct statements among (I) to (IV) regarding silicones are:

I. They are polymers with hydrophobic character.
II. They are biocompatible.
III. In general, they have high thermal stability and low dielectric strength.
IV. Usually, they are resistant to oxidation and used as greases.

(a) I and II only **[2019, 9 Jan Shift-I]**
(b) I, II, III only
(c) I, II, III and IV
(d) I, II and IV only

Ans. ***(d)***

Silicones are polysiloxanes with general chemical formula, $[R_2SiO]_n$, where R is an organic group such as: — CH_3, — C_2H_5, — C_6H_5 etc.

Silicones have many useful properties:

(i) They repel water and form watertight seals.
(ii) They are heat resistant because of constancy of properties over a wide range of temperature (– 100° to 250° C).
(iii) Silicones are non-toxic.
(iv) Silicones are biocompatible because these do not support microbiological growth and these have high gas permeability at room temperature.
(v) They are resistant to O_2, O_3 and UV-radiation.
(vi) Silicones are formulated to be electrically insulative.
(vii) Silicone grease is typically used as a lubricant for brake components in automobiles, since it is stable at high temperature, is not water soluble and is a odourless viscous liquid.

34 The element that shows greater ability to form $p\pi$-$p\pi$ multiple bonds, is **[2019, 12 Jan Shift-II]**

(a) Ge (b) Si
(c) Sn (d) C

Ans. ***(d)***

Carbon (C) has greatest ability to form stable $p\pi$-$p\pi$ multiple bonds. 2*p*-orbitals of this element participate in the process. The stability of multiple bonds of C is attributed to their closeness with C-nucleus. Thus, the smaller size of C plays a significant role in the process.

35 The element that does not show catenation is **[2019, 12 Jan Shift-II]**

(a) Ge (b) Sn
(c) Si (d) Pb

Ans. ***(d)***

The property of self-linking of atoms of an element through covalent bonds to form straight or branched chains and rings of different sizes is called catenation. Down the group, catenation tendency decreases due to decrease in element bond strength. Carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb) are group-14 elements.

Catenation tendency is highest in carbon while silicon has second highest tendency of catenation among all elements of family due to higher bond energy. The decreasing tendency of catenation among group 14 elements is as follows:

$$C >> Si > Ge \approx Sn$$

However, Pb does not show catenation.

36 Which of the following exists as covalent crystals in the solid state? **[JEE Main 2013]**

(a) Iodine (b) Silicon
(c) Sulphur (d) Phosphorus

Ans. ***(b)***

Silicon exists as covalent crystal in solid state. It exhibits a network structure like diamond.

37 Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is **[AIEEE 2007]**

(a) R_4Si (b) $R\,SiCl_3$
(c) R_2SiCl_2 (d) R_3SiCl

Ans. ***(b)***

$R\,SiCl_3$ give cross linked silicone polymer on hydrolysis.

38 The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence **[AIEEE 2007]**

(a) $GeX_2 < SiX_2 < SnX_2 < PbX_2$
(b) $SiX_2 < GeX_2 < PbX_2 < SnX_2$
(c) $SiX_2 < GeX_2 < SnX_2 < PbX_2$
(d) $PbX_2 < SnX_2 < GeX_2 < SiX_2$

Ans. ***(c)***

Inert pair effect becomes predominant due to which +2 oxidation state becomes more stable down the group and hence, the stability of dihalides increases down the group.

$$SiX_2 < GeX_2 < SnX_2 < PbX_2$$

39 Which of the following oxides is amphoteric in character? **[AIEEE 2005]**

(a) SnO_2 (b) SiO_2
(c) CO_2 (d) CaO

Ans. ***(a)***

A species is amphoteric, if it is soluble in acid (behave as a base) as well as in base (behave as an acid).

$$\underset{\text{Base}}{SnO_2} + 4HCl \longrightarrow SnCl_4 + 2H_2O$$
$$\underset{\text{Acid}}{\quad}$$

$$\underset{\text{Acid}}{SnO_2} + 2NaOH \longrightarrow \underset{\text{Base}}{Na_2SnO_3} + H_2O$$

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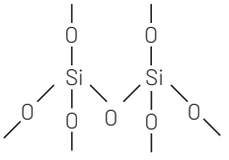
40 In silicon dioxide **[AIEEE 2005]**

(a) there are double bonds between silicon and oxygen atoms
(b) silicon atom is bonded to two oxygen atoms
(c) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
(d) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms

Ans. ***(d)***

In SiO_2, each silicon atom is bonded to four oxygen atoms, that are arranged tetrahedrally around it and each O – atom is attached to two silicon atoms by covalent bonds.



41 The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to **[AIEEE 2004]**

(a) a change in the crystalline structure of tin
(b) an interaction with nitrogen of the air at very low temperature
(c) a change in the partial pressure of oxygen in the air
(d) an interaction with water vapour contained in the humid air

Ans. ***(a)***

As temperature decreases, white tin (β -form changes to grey tin (α-form).

$$\alpha\text{-Sn} \underset{}{\overset{13.2^\circ C}{\rightleftharpoons}} \beta\text{-Sn}$$

α-Sn has a much lower density.

42 Glass is a **[AIEEE 2003]**

(a) microcrystalline solid
(b) super cooled liquid
(c) gel
(d) polymeric mixture

Ans. ***(b)***

Glass is a supercooled liquid, which forms a non-crystalline solid. The common lime-soda glass used for bottles and jars is a supercooled mixture of sodium and calcium silicates.

43 Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite

(a) is a non-crystalline substance
(b) is an allotropic form of diamond
(c) has molecules of variable molecular masses like polymers
(d) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds **[AIEEE 2003]**

Ans. ***(d)***

C-atoms of graphite form covalently bonded plates (layers). These layers are held together by weak forces of attraction.

i.e., one layer can slide over other to cause lubricacy. It cannot be melted easily as large number of atoms being bonded strongly in the layer to form big entity.

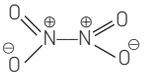
TOPIC 3
Group 15 Elements

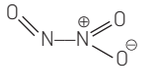
44 The oxide without nitrogen-nitrogen bond is **[2021, 1 Sep Shift-II]**

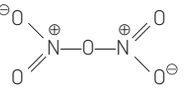
(a) N_2O (b) N_2O_4 (c) N_2O_3 (d) N_2O_5

Ans. ***(d)***

(a) Structure of N_2O $\longrightarrow$ $N\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$

(b) Structure of N_2O_4 $\longrightarrow$ 

(c) Structure of N_2O_3 $\longrightarrow$ 

(d) Structure of N_2O_5 $\longrightarrow$ 

The oxide without nitrogen-nitrogen bond is N_2O_5.

45 Which one of the following is formed (mainly) when red phosphorus is heated in a sealed tube at 803 K ? **[2021, 27 Aug Shift-II]**

(a) White phosphorus
(b) Yellow phosphorus
(c) β-black phosphorus
(d) α-black phosphorus

Ans. ***(d)***

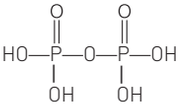
When red phosphorus is heated in a sealed tube at 803 K, α-black phosphorus is formed. Therefore , option (d) is correct.

46 The oxidation states of 'P' in $H_4P_2O_7$, $H_4P_2O_5$ and $H_4P_2O_6$, respectively are **[2021, 27 July Shift-I]**

(a) 7, 5 and 6 (b) 5, 4 and 3
(c) 5, 3 and 4 (d) 6, 4 and 5

Ans. ***(c)***

$H_4P_2O_7$



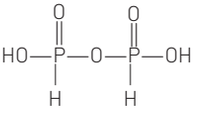
Oxidation state of 'P' in $H_4P_2O_7$

$\rightarrow 4(+1) + 2x + 7(-2) = 0$

$2x - 10 = 0$

$x = +5$

$H_4P_2O_5$



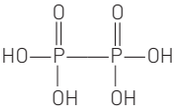
Oxidation state of P in $H_4P_2O_5$

$\rightarrow 4(+1) + 2x + 5(-2) = 0$

$2x - 6 = 0$

$x = +3$

$H_4P_2O_6$



Oxidation state of P in $H_4P_2O_6$

$\rightarrow 4(+1) + 2x + 6(-2) = 0$

$2x - 8 = 0$

$x = +4$

Hence, oxidation state of P in and are 5, 3 and 4 respectively.

47 Which one of the following group-15 hydride is the strongest reducing agent ? **[2021, 22 July Shift-II]**

(a) AsH_3 (b) BiH_3
(c) PH_3 (d) SbH_3

Ans. ***(b)***

BiH_3 is a strongest reducing agent among group-15, as we move down the group reducing strength of hydride increases.

Reason As we move down the group, the *M*—H bond can break more easily to evolve H_2 gas which acts as the reducing agent. Thus, BiH_3 is least stable among the hydrides of group 15 and hence is the strongest reducing agent.

Reducing nature of hydride

$$\propto \frac{1}{\text{Thermal stability (or) bond strength}}$$

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Order of thermal stability bond strength :

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Order of reducing nature

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

48 Chemical nature of the nitrogen oxide compound obtained from a reaction of concentrated nitric acid and P_4O_{10} (in 4 : 1 ratio) is

[2021, 20 July Shift-I]

(a) acidic (b) basic
(c) amphoteric (d) neutral

Ans. ***(a)***

Chemical nature of the nitrogen pentaoxide compound obtained from a reaction of concentrated nitric acid and P_4O_{10} (in 4 : 1 ratio) is acidic.

Chemical reaction is as follows

$$\underset{\text{Phosphorus pentaoxide}}{P_4O_{10}} + \underset{\text{Nitric acid}}{4HNO_3} \longrightarrow \underset{\text{Meta-phosphoric acid}}{4HPO_3} + \underset{\substack{\text{Nitrogen pentaoxide}\\(\text{Acidic})}}{2N_2O_5}$$

$\therefore N_2O_5$ is an acidic oxide.

49 The oxidation states of nitrogen in NO, NO_2, N_2O and NO_3^- are in the order of **[2021, 18 March Shift-II]**

(a) $NO_3^- > NO_2 > NO > N_2O$

(b) $NO_2 > NO_3^- > NO > N_2O$

(c) $N_2O > NO_2 > NO > NO_3^-$

(d) $NO > NO_2 > N_2O > NO_3^-$

Ans. ***(a)***

Oxidation states of 'N' in the given compounds are as follows

$NO \rightarrow x + 1(-2) = 0$

$x = +2$

$NO_2 \rightarrow x + 2\times(-2) = 0$

$x = +4$

$N_2O \rightarrow 2x + (-2) = 0$

$x = +1$

$NO_3^- \rightarrow x + 3(-2) = -1$

$\Rightarrow \quad x = +5$

Decreasing order of oxidation state of 'N' is as follows

$NO_3^- > NO_2 > NO > N_2O$.

50 The number of ionisable hydrogens present in the product obtained from a reaction of phosphorus trichloride and phosphonic acid is

[2021, 18 March Shift-I]

(a) 3 (b) 0 (c) 2 (d) 1

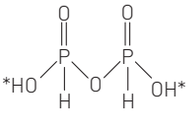
Ans. ***(c)***

$PCl_3 + H_3PO_3 + H_2O \longrightarrow H_4P_2O_5 + HCl$

Phosphorus trichloride + Phosphonic acid → Pyrophosphoric acid + Hydrochloric acid

Product is pyrophosphoric acid, i.e. $H_4P_2O_5$.

The structure of pyrophosphoric acid shows that it has two acidic or ionisable hydrogen, i.e. *H.



(Two ionisable H)

51 The set that represents the pair of neutral oxides of nitrogen is

[2021, 17 March Shift-II]

(a) NO and N_2O (b) N_2O and N_2O_3
(c) N_2O and NO_2 (d) NO and NO_2

Ans. ***(a)***

N_2O and NO are neutral oxides of nitrogen, whereas NO_2 and N_2O_3 are acidic oxides.

Neutral oxides are neither acidic nor basic. These oxides neither react with acids nor with bases.

52 Which of the following compound cannot act as a Lewis base?

[2021, 17 March Shift-I]

(a) NF_3 (b) PCl_5 (c) SF_4 (d) ClF_3

Ans. ***(b)***

PCl_5 has no lone-pair on the central atom but has empty *d*-orbital in valence shell, so that it can accept a pair of electrons (from a Lewis base). So, PCl_5 act as a Lewis acid.

Lewis acid Species which accepts a pair of electron in their vacant orbital e.g. BF_3, $AlCl_3$, PCl_5.

Lewis base Species which can donate a pair of electron, e.g.

$\ddot{P}Cl_3$, $\ddot{N}H_3$, $\ddot{N}F_3$, $:\ddot{C}lF_3$, $\ddot{S}F_4$.

53 The reaction of white phosphorus on boiling with alkali in inert atmosphere resulted in the formation of product *A*. The reaction of 1 mol of *A* with excess of $AgNO_3$ in aqueous medium gives ..... mol(es) of Ag (Round off to the nearest integer).

[2021, 17 March Shift-I]

Ans. ***(4)***

Reaction of white phosphorus with alkali in inert atmosphere forms sodium hypophosphite (NaH_2PO_2).

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{(A)\ \text{Sodium hypophosphite}}{3NaH_2PO_2} + PH_3$$

1 mole of NaH_2PO_2 reacts with excess of $AgNO_3$ in aqueous medium to give 4 moles of Ag.

$NaH_2PO_2 + 4AgNO_3 + 2H_2O \longrightarrow 4Ag + H_3PO_4 + NaNO_3 + 3HNO_3$

Hence, 1 mole produce 4 moles of Ag.

54 **Statement I** Sodium hydride can be used as an oxidising agent.

Statement II The lone pair of electrons on nitrogen in pyridine makes it basic.

Choose the correct answer from the options given below.

[2021, 16 March Shift-II]

(a) Both statement I and statement II are true
(b) Both statement I and statement II are false
(c) Statement I is true but statement II is false
(d) Statement I is false but statement II is true

Ans. ***(c)***

NaH is not an oxidising agent as Na^+ and H^- ions are formed. Na exists only in + 1 and hydrogen is present in minimum –1 state so, cannot be reduced further. NaH is used as reducing agent.

Lone pair on nitrogen in pyridine is localised and does not take part in resonance. So, it can accept H^+ acting as a base.

Pyridine

So, statement I is true but statement II is false.

55 A group 15 element, which is a metal and forms a hydride with strongest reducing power among group 15 hydrides. The element is

[2021, 16 March Shift-I]

(a) Sb (b) P
(c) As (d) Bi

Ans. ***(d)***

BiH_3 is the strongest reducing agent and have strongest reducing power. The reducing character of the group 15 element hydrides increases down the group. Ammonia is only a mild reducing

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agent while BiH_3 is the strongest reducing agent amongst all the hydrides. This is due to the decrease in bond energy down the group.

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
$\Delta_{diss.}H$ kJ/mol^{-1}	389	322	297	255	

(Increase in reducing power)

So, correct answer is Bi (bismuth).

56 Find *A*, *B* and *C* in the following reactions:

$$NH_3 + A + CO_2 \longrightarrow (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + H_2O + B \rightarrow NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + C$$

[2021, 26 Feb Shift-I]

(a) *A* – O_2 , *B* – CO_2 , *C* – Na_2CO_3
(b) *A* – H_2O , *B* – O_2 , *C* – Na_2CO_3
(c) *A* – H_2O, *B* – O_2, *C* – $NaHCO_3$
(d) *A* – H_2O, *B* – CO_2, *C* – $NaHCO_3$

Ans. ***(d)***

The given reaction take place as follows

(i) Ammonia (NH_3) reacts with H_2O and CO_2 to give ammonium carbonate [$(NH_4)_2CO_3$].

$$\underset{(A)}{2NH_3 + H_2O} + CO_2 \longrightarrow (NH_4)_2CO_3$$

(ii) Ammonium carbonate react with water (H_2O) and CO_2 to give ammonium hydrogen carbonate (NH_4HCO_3).

$$(NH_4)_2CO_3 + H_2O + \underset{(B)}{CO_2} \longrightarrow 2NH_4HCO_3$$

(iii) Ammonium hydrogen carbonate reacts with sodium chloride (NaCl) to give ammonium chloride (NH_4Cl) along with sodium bicarbonate ($NaHCO_3$).

$$NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + \underset{(C)}{NaHCO_3}$$

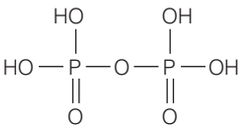
So, *A* - H_2O, *B* - CO_2 ; *C* - $NaHCO_3$.

57 In a molecule of pyrophosphoric acid, the number of P—OH, P═O and P—O—P bonds/moiety(ies) respectively are **[2020, 3 Sep Shift-I]**

(a) 2, 4 and 1 (b) 3, 3, and 3
(c) 4, 2, and 0 (d) 4, 2, and 1

Ans. ***(d)***

The structure of pyrophosphoric acid ($H_4P_2O_7$) molecule is



Number of P—OH moieties = 4, P ═ O bonds = 2 and P—O —P bond = 1.

58 Reaction of ammonia with excess Cl_2 gives **[2020, 5 Sep Shift-II]**

(a) NH_4Cl and N_2
(b) NH_4Cl and HCl
(c) NCl_3 and NH_4Cl
(d) NCl_3 and HCl

Ans. ***(d)***

A yellow explsive liquid *n*drogen trichloride is formed

$$N + \underset{\text{(Excess)}}{3Cl_2} \longrightarrow 3HCl + \underset{\substack{\text{Nitrogen}\\ \text{trichloride}}}{NCl_3}$$

It here ammonia is taken in excess then ammonium chloride is formed.

$$\underset{\text{(Excess)}}{7NH_3} + 3Cl_2 \longrightarrow NH_4Cl + N_2$$

59 The correct statement with respect to dinitrogen is **[2020, 6 Sep Shift-I]**

(a) N_2 is paramagnetic in nature.
(b) it can combine with dioxygen at 25°C.
(c) liquid dinitrogen is not used in cryosurgery.
(d) it can be used as an inert diluent for reactive chemicals.

Ans. ***(d)***

(a) All electrons in N_2 are paired, thus it is diamagnetic, not paramagnetic.

(b) $N_2 + O_2 \underset{}{\overset{\text{Above } 2000^\circ C}{\rightleftharpoons}} 2NO(g)$,

(c) Liquid N_2 gas is used to create extremely cold temperature to distroy diseased tissues located outside the body.

(d) N_2 gas used as a diluent due to it's inert nature.

Hence, the correct option is (d).

60 The reaction of NO with N_2O_4 at 250 K gives **[2020, 6 Sep Shift-II]**

(a) N_2O (b) NO_2 (c) N_2O_3 (d) N_2O_5

Ans. ***(c)***

Nitrogen monoxide react with dinitrogen tetraoxide at 250 K temperature forms blue solid.

$$2NO + N_2O_4 \xrightarrow{250\,K} 2N_2O_3$$

N_2O_3 is acidic in nature. In N_2O_3, N has +3 oxidation state. Generally, oxides with higher oxidation states are more acidic than oxides having lower oxidation state. It is a blue solid because it strongly absorbs in the visible region to appear bright blue in colour.

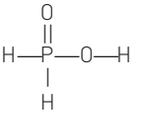
61 White phosphorus on reaction with concentrated NaOH solution in an inert atmosphere of CO_2 gives phosphine and compound (*X*). (*X*) on acidification with HCl gives compound (*Y*). The basicity of compound (*Y*) is **[2020, 8 Jan Shift-II]**

(a) 4 (b) 3 (c) 2 (d) 1

Ans. ***(d)***

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{(X)}{3NaH_2PO_2}$$
$$\downarrow +3HCl$$
$$\underset{(Y)}{3H_3PO_2} + 3NaCl$$

H_3PO_2 (*Y*) is a monobasic acid. Here, the H-atom of OH group is ionisable and cause the basicity.



62 The correct order of the oxidation states of nitrogen in NO, NO_2, NO_2 and N_2O_3 is **[2019, 9 April Shift-I]**

(a) $NO_2 < NO < N_2O_3 < N_2O$
(b) $N_2O < NO < N_2O_3 < NO_2$
(c) $O_2 < N_2O_3 < NO < N_2O$
(d) $N_2O < N_2O_3 < NO < NO_2$

Ans. ***(b)***

The correct increasing order of oxidation state of nitrogen for nitrogen oxides is

$$\overset{+1}{N}_2O < \overset{+2}{N}O < \overset{+3}{N}_2O_3 < \overset{+4}{N}O_2$$

Oxidation state of N in N_2O is

$$2(x) - 2 = 0;\ x = +\frac{2}{2} = +1$$

Oxidation state of N in NO is

$$x - 2 = 0;\ x = +2$$

Oxidation state of N in N_2O_3 is

$$2x + 3(-2) = 0;\ x = \frac{6}{2} = 3$$

Oxidation state of N in NO_2 is

$$x + 2(-2) = 0;\ x - 4 = 0;\ x = +4$$

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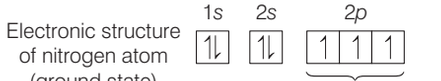
63 The correct statement among the following is **[2019, 12 April Shift-I]**

(a) $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$.
(b) $(SiH_3)_3N$ is pyramidal and more basic than $(CH_3)_3N$.
(c) $(SiH_3)_3N$ is pyramidal and less basic than $(CH_3)_3N$.
(d) $(SiH_3)_3N$ is planar and more basic than $(CH_3)_3N$.

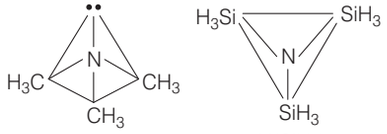
Ans. ***(d)***

The correct statement is that $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$. The compounds trimethylamine $(CH_3)_3N$ and trisilylamine $(SiH_3)_3N$ have similar formulae, but have totally different structures.

In trimethylamine the arrangement of electrons is as follows :



In trisilylamine, three sp^2 orbitals are used for σ -bonding, giving a plane triangular structure.



$N(CH_3)_3$ molecule $N(SiH_3)_3$ molecule

64 An organic compound *A* is oxidised with Na_2O_2 followed by boiling with HNO_3. The resultant solution is then treated with ammonium molybdate to yield a yellow precipitate.

Based on above observation, the element present in the given compound is **[2019, 12 April Shift-I]**

(a) nitrogen
(b) phosphorus
(c) fluorine
(d) sulphur

Ans. ***(b)***

Organic compound 'A' contain phosphorus as it gives positive test with ammonium molybdate. Phosphorus present in organic compound 'A' get oxidised with Na_2O_2 and form Na_3PO_4.

$$2P + 5Na_2O_2 \longrightarrow 2Na_3PO_4 + 2Na_2O$$

Compound Sodium phosphate

Na_3PO_4 in presence of HNO_3 form H_3PO_4 and $NaNO_3$.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

Upon cooling, a few drops of ammonium molybdate solution are added. A yellow ppt. confirms the presence of phosphorus in the organic compound.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3PO_4.12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$$

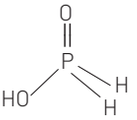
Yellow ppt

65 Good reducing nature of H_3PO_2 is attributed to the presence of **[2019, 9 Jan Shift-II]**

(a) two P—H bonds
(b) one P—H bond
(c) two P—OH bonds
(d) one P—OH bond

Ans.***(a)***

The structure of H_3PO_2 (hypophosphorous) acid is



Due to the presence of two P—H bonds, H_3PO_2 acts a strong reducing agent. e.g.,

$$4\overset{+1}{Ag}NO_3 + H_3\overset{+1}{P}O_2 + 2H_2O \longrightarrow 4\overset{0}{Ag}\downarrow + H_3\overset{+5}{P}O_4 + 4HNO_3$$

66 The metal that forms nitride by reacting directly with N_2 of air, is **[2019, 9 Jan Shift-II]**

(a) Rb (b) K
(c) Cs (d) Li

Ans. ***(d)***

Among the group-1 metals, only Li is able to form its nitride, Li_3N. [All alkaline earth metals of group-2 form their nitride, M_3N_2]

$$6Li + N_2 \longrightarrow 2Li_3N \text{ (Ruby red solid)}$$

(Air)

I II

$$[3M + N_2 \longrightarrow M_3N_2]$$

$Li^{\oplus}$ is the smallest metal ion of group-1. Smaller size of $Li^{\oplus}$ and larger size of nitride ion, N^{3-}, enable $Li^{\oplus}$ to polarise the spherical electron cloud of N^{3-} and it gives higher stability to Li_3N.

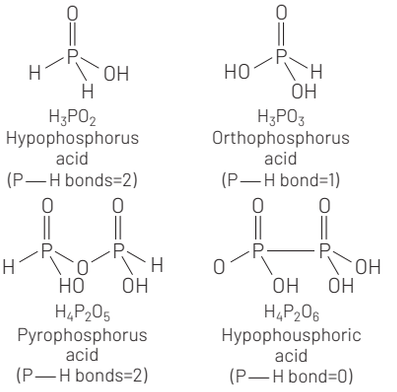
67 The pair that contains two P—H bonds in each of the oxoacids is

(a) $H_4P_2O_5$ and $H_4P_2O_6$
(b) H_3PO_3 and H_3PO_2
(c) $H_4P_2O_5$ and H_3PO_3
(d) H_3PO_2 and $H_4P_2O_5$

[2019, 10 Jan Shift-II]

Ans. ***(d)***

Let us consider the structure of the phosphorus oxyacids,



68 The compound that does not produce nitrogen gas by the thermal decomposition is **[JEE Main 2018]**

(a) $Ba(N_3)_2$ (b) $(NH_4)_2Cr_2O_7$
(c) NH_4NO_2 (d) $(NH_4)_2SO_4$

Ans. ***(d)***

The thermal decomposition of given compounds is shown below

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$$

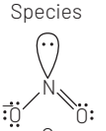
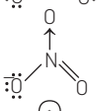
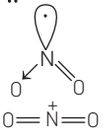
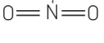
$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

Thus, only $(NH_4)_2SO_4$ does not gives N_2 on heating (It give NH_3). While rest of the given compounds gives N_2 on their thermal decomposition.

69 The species in which the N-atom is in a state of *sp* hybridisation is **[JEE Main 2016]**

(a) NO_2^- (b) NO_3^-
(c) NO_2 (d) NO_2^+

Ans. ***(d)***

Species	Hybridisation
	sp^2
	sp^2
	sp^2
	sp

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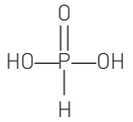
70 The pair in which phosphorus atoms have a formal oxidation state of +3 is **[JEE Main 2016]**

(a) pyrophosphorous and hypophosphoric acids
(b) orthophosphorous and hypophosphoric acids
(c) pyrophosphorous and pyrophosphoric acids
(d) orthophosphorous and pyrophosphorous acids

Ans. ***(d)***

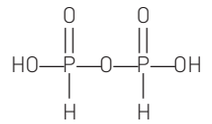
Orthophosphorous acid, H_3PO_3 :



$H_3\overset{x}{P}O_3 = 3 + x + 3(-2) = 0$ or $x = +3$

Pyrophosphorous acid,

$H_4P_2O_5$:



$H_4\overset{x}{P}_2O_5 = 4 + 2x + 5(-2) = 0$

$4 + 2x - 10 = 0 \Rightarrow x = +3$

71 Which one of the following properties is not shown by NO? **[JEE Main 2014]**

(a) It is diamagnetic in gaseous state
(b) It is a neutral oxide
(c) It combines with oxygen to form nitrogen dioxide
(d) Its bond order is 2.5

Ans. ***(a)***

The electronic configuration of NO[15 e^-] is given by

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_z^1$

Thus, NO possess one unpaired electron, hence, it is paramagnetic in nature. However, it dimerises at low temperature to become diamagnetic.

$$2NO \rightleftharpoons N_2O_2$$

Bond order of NO $= \frac{1}{2}[10 - 5] = 2.5$

Thus, bond order of NO is 2.5 and it combines with O_2 to give NO_2.

Hence, the correct option is (a).

72 Which of the following statements is wrong?

(a) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the periodic table
(b) Nitrogen can't form $d\pi$-$p\pi$ bond
(c) Single N—N bond is weaker than the single P—P bond
(d) N_2O_4 has two resonance structure **[AIEEE 2011]**

Ans. ***(a)***

(a) Thermal stability of the hydrides decrease as we go down the group in periodic table for group 15 (N-family)

$BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

Least stable — Most stable

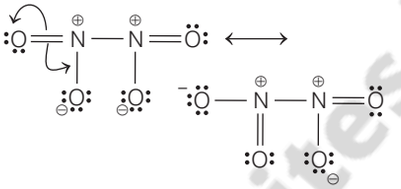
M-H	—	255	247	322	391

Bond-energy (kJ mol^{-1})

(b) Due to absence of *d*-orbital, nitrogen can't form $d\pi - p\pi$ bond, thus it is correct.

(c) The N-N bond (BE 160 kJ mol^{-1}) is weaker than P-P bond (BE 209 kJ mol^{-1}). Thus, it is correct.

(d) N_2O_4 can form two resonance structures



Thus, it is correct.

73 The bond dissociation energy of B—F in BF_3 is 646 kJ mol^{-1} whereas that of C—F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B—F bond dissociation energy as compared to that of C—F is **[AIEEE 2009]**

(a) smaller size of B-atom as compared to that of C-atom
(b) stronger σ-bond between B and F in BF_3 as compared to that between C and F in CF_4
(c) significant $p\pi$ - $p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4
(d) lower degree of $p\pi$ - $p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4

Ans. ***(c)***

Due to identical sizes of 2*p*–orbitals on *B* and *F*, back donation of a lone pair of electrons from the filled 2*p*– orbital of F to the empty 2*p*-orbital of *B* occurs to a considerable extent.

As a result, B—F bond has some double bond character and hence, bond dissociation energy of B—F bond in BF_3 is much higher that of C—F bond in CF_4. This is due to the absence of empty 2*p*– orbital and hence, back donation does not occur.

74 In which of the following arrangements, the sequence is not strictly according to the property written against it? **[AIEEE 2009]**

(a) $CO_2 < SiO_2 < SnO_2 < PbO_2$ increasing oxidising power
(b) HF < HCl < HBr < HI increasing acid strength
(c) $NH_3 > PH_3 < AsH_3 < SbH_3$ increasing basic strength
(d) B < C < O < N increasing first ionisation enthalpy

Ans. ***(c)***

The correct increasing basic strength

$SbH_3 < AsH_3 < PH_3 < NH_3$

NH_3 is most basic because of its small size, the electron density of electron pair is concentrated over small region.

As the size increases, the electron density gets diffused over a large surface area and hence the ability to donate the electron pair (basicity) decreases. Hence, basic strength decreases down the group.

75 Regular use of which of the following fertilizers increases the acidity of soil ? **[AIEEE 2007]**

(a) Potassium nitrate
(b) Urea
(c) Superphosphate of lime
(d) Ammonium sulphate

Ans. ***(d)***

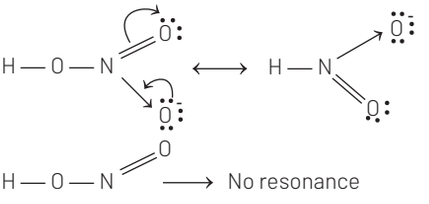
$(NH_4)_2SO_4 \longrightarrow \underset{\text{Acidic}}{2NH_4^+} + SO_4^{2-}$

76 Which of the following statements is true ? **[AIEEE 2006]**

(a) H_3PO_3 is a stronger acid than H_2SO_3
(b) In aqueous medium, HF is a stronger acid than HCl
(c) $HClO_4$ is weaker acid than $HClO_3$
(d) HNO_3 is a stronger acid than HNO_2

Ans. ***(d)***

Conjugate base of HNO_3 is resonance stablised than that of HNO_2. Hence, HNO_3 is stronger acid than HNO_2.



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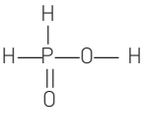
77 The number of hydrogen atom(s) attached to phosphorus atom in hypophosphorous acid is **[AIEEE 2005]**

(a) three (b) one (c) two (d) zero

Ans. ***(c)***

Hypophosphorous acid (H_3PO_2) is a monobasic acid and has only one ionisable H because two H-atoms are directly attached to phosphorus. Thus, the correct statement is (c).

The structure of H_3PO_2 is



attached to O.

78 Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in the alkaline solutions but not in acidic solutions. What is the reason for it? **[AIEEE 2003]**

(a) In acidic solutions, hydration protects copper ions

(b) In acidic solutions, protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available

(c) In alkaline solutions, insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali

(d) Copper hydroxide is an amphoteric substance

Ans. ***(b)***

In acidic solutions, N atoms of NH_3 donates their lone pair electrons to protons forming NH_4^+ ions. Therefore, lone pair electrons of NH_3 are not available for forming the complex with copper ions.

79 What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid? **[AIEEE 2003]**

(a) Cr^{3+} and $Cr_2O_7^{2-}$ are formed

(b) $Cr_2O_7^{2-}$ and H_2O are formed

(c) CrO_4^{2-} is reduced to +3 state of Cr

(d) None of the above

Ans. ***(b)***

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

80 The metallic sodium dissolves in liquid ammonia to form a deep blue coloured solution. The deep blue colour is due to the formation of **[AIEEE 2002]**

(a) solvated electron $e^-(NH_3)_x$

(b) solvated atomic sodium, $Na(NH_3)_y$

(c) $(Na^+ + Na^-)$

(d) $NaNH_2 + H_2$

Ans. ***(a)***

All alkali metals dissolve in liquid ammonia and gives solvated ammoniated electrons.

$$M + (x + y)NH_3 \rightarrow M^+(NH_3)_x + e^-(NH_3)_y$$

These electrons are excited to higher energy levels and the absorption of photons occurs in the red region of the spectrum. Thus, solution appears blue.

81 PCl_3 and PCl_5 both exist; NCl_3 exists but NCl_5 does not exist. It is due to **[AIEEE 2002]**

(a) lower electronegativity of P than N

(b) lower tendency of N to form covalent bond

(c) availability of vacant *d*-orbital in P but not in N

(d) statement is itself incorrect

Ans. ***(c)***

Phosphorus (3rd period element) can raise covalency facilitating vacant *d*-orbitals

P(ground) $[Ne]3s^2 \;\; 3p^3 \;\; 3d^0$

P(excited) $[Ne]3s^1 \;\; 3p^3 \;\; 3d^1$

TOPIC 4
Group 16 Elements

82 Number of paramagnetic oxides among the following given oxides is Li_2O, Na_2O_2, KO_2, HgO and K_2O **[2021, 1 Sep Shift-II]**

(a) 1 (b) 2

(c) 3 (d) 0

Ans. ***(a)***

For the oxides Li_2O, CaO, Na_2O_2, KO_2, MgO and K_2O,

$$Li_2O \Rightarrow O^{2-}$$
$$CaO \Rightarrow O^{2-}$$
$$Na_2O_2 \Rightarrow O_2^{2-}$$
$$KO_2 \Rightarrow O_2^-$$
$$MgO \Rightarrow O^{2-}$$
$$K_2O \Rightarrow O^{2-}$$

$\therefore$ Electronic configuration of O_2^{2-} molecule is

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^2 \approx \pi^* 2p_y^2$

Hence, O_2^{2-} is diamagnetic in nature as no unpaired electron is present.

Electronic configuration of O^{2-} is : $1s^2, 2s^2, 2p^6$

Hence, O^{2-} is also diamagnetic.

Electronic configuration of O_2^- is :

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2 \approx \pi 2p_z^2, \pi^* 2p_y^2 \approx \pi^* 2p_z^1$

Since, unpaired electron is present in $\pi^* 2p_z$ orbital.

Therefore, O_2^- is paramagnetic in nature.

$\therefore$ Only KO_2 is paramagnetic oxide.

83 The depositions of *X* and *Y* on ground surfaces is referred to as wet and dry depositions, respectively. *X* and *Y* are **[2021, 31 Aug Shift-II]**

(a) *X* = Ammonium salts, *Y* = CO_2

(b) *X* = SO_2, *Y* = Ammonium salts

(c) *X* = Ammonium salts, *Y* = SO_2

(d) *X* = CO_2, *Y* = SO_2

Ans. ***(c)***

Oxides of nitrogen and sulphur are acidic and settle down on ground as dry deposition.

Ammonium salts in rain drops result in wet deposition.

$\therefore$ *X* = Ammonium salts

Y = SO_2

84 Consider the sulphides HgS, PbS, CuS, Sb_2S_3, As_2S_3 and CdS. Number of these sulphides soluble in 50% HNO_3 is **[2021, 31 Aug Shift-I]**

Ans. ***(4)***

PbS, CuS, As_2S_3, CdS, are soluble in 50% HNO_3 while HgS, Sb_2S_3 are insoluble in 50% HNO_3.

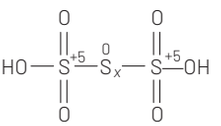
85 In polythionic acid, $H_2S_xO_6$ ($x = 3$ to 5) the oxidation state(s) of sulphur is/are **[2021, 27 Aug Shift-I]**

(a) only + 5 (b) only + 6

(c) + 3 and + 5 (d) 0 and + 5

Ans. ***(d)***

Polythionic acid with a small number of sulphur atoms (3 to 5) are most stable. The oxidation state of sulphur in polythionic acid are 0 and +5 only. They have straight chain of sulphur.



where $x = 3$ to 5.

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86 The product obtained from the electrolytic oxidation of acidified sulphate solutions, is **[2021, 27 July Shift-I]**

(a) HSO_4^- (b) HO_3SOOSO_3H
(c) HO_2SOSO_2H (d) HO_3SOSO_3H

Ans. ***(b)***

Electrolysis of concentrated solution of acidified sulphate solution yields peroxydisulphuric acid ($H_2S_2O_8$).

During electrolysis,

At cathode

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2 \uparrow$$

At anode

$$2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$$
$$2H_2O \longrightarrow 4H^+ + O_2 + 2e^-$$

87 Chalcogen group elements are **[2021, 26 Aug Shift-II]**

(a) Se, Tb and Pu (b) Se, Te and Po
(c) S, Te and Pm (d) O, Ti and Po

Ans. ***(b)***

Oxygen family is also known as chalcogen family.

O, Se, S, Te and Po are chalcogen family member.

88 Match List -I with List II.

	List-I (Industrial process)		List-II (Application)
A.	Haber's process	(i)	HNO_3 synthesis
B.	Ostwald's process	(ii)	Aluminium extraction
C.	Contact process	(iii)	NH_3 synthesis
D.	Hall-Heroult process	(iv)	H_2SO_4 synthesis

Choose the correct answer from the options given below : **[2021, 16 March Shift-I]**

(a) A-(ii), B-(iii), C-(iv), D-(i)
(b) A-(iii), B-(iv), C-(i), D-(ii)
(c) A-(iii), B-(i), C-(iv), D-(ii)
(d) A-(iv), B-(i), C-(ii), D-(iii)

Ans. ***(c)***

A. Haber's process - NH_3 synthesis

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

B. Ostwald's process - HNO_3 synthesis

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
$$4NO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 4HNO_3(aq)$$

C. Contact process - H_2SO_4 synthesis

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$
$$SO_3(g) + H_2SO_4(aq) \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7(l)}$$
$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$$

D. Hall-Heroult process- Aluminium extraction

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

Correct match is,

A → (iii), B → (i), C → (iv), D → (ii)

89 The correct order of electron gain enthalpy is **[2021, 26 Feb Shift-II]**

(a) S > Se > Te > O (b) Te > Se > S > O
(b) O > S > Se > Te (d) S > O > Se > Te

Ans. ***(a)***

Oxygen is the second most electronegative element in comparison to fluorine. In group -16 family (O, S, Se, Te), O-atom is smallest in size. So, electron density on O-atom is very high in group -16 .

During addition of a free electron to gaseous O-atom,

$$O(g) + e^- \longrightarrow O^-(g)$$

We have to supply a significant amount of energy (endothermic) to overcome the electrostatic repulsion between the approaching electron and O-atom of very high electron density. So, the net value of electron affinity (EA) or (negative) electron gain enthalpy [$\Delta_{eg}H$ or $|\Delta_{eg}H|$] of oxygen decreases to a higher extent in comparison to other elements of group -16 who have larger size and lower electronegativity.

So, the correct order of EA or $|\Delta_{eg}H|$ of group -16 elements will be

S > Se > Te > O.

90 Given below are two statements.

Statement I α and β-forms of sulphur can change reversibly between themselves with slow heating or slow cooling.

Statement II At room temperature, the stable crystalline form of sulphur is monoclinic sulphur.

In the light of the above statements, choose the correct answer from the options given below. **[2021, 25 Feb Shift-II]**

(a) Both statements I and II are true.
(b) Both statements I and II are false.
(c) Statement I is true but statement II is false.
(d) Statement I is false but statement II is true.

Ans. ***(c)***

Two crystalline allotropic forms of sulphur (S_α and S_β) can change reversibly between themselves with slow heating (above 369 K) or cooling.

$$\underset{\text{(Rhombic)}}{S_\alpha} \underset{\text{Cooling}}{\overset{> 369\ K}{\rightleftharpoons}} \underset{\text{(Monoclinic)}}{S_\beta}$$

So, statement I is true.

At room temperature or at standard conditions of pressure and temperature, rhombic sulphur is the thermodynamically most stable crystalline allotrope of sulphur ($\Delta_f H^\circ = 0$).

So, statement II is false.

91 Among the following allotropic forms of sulphur, the number of allotropic forms, which will show paramagnetism is ..... . **[2021, 24 Feb Shift-II]**

(a) α-sulphur (b) β-sulphur
(c) S_2-form

Ans. ***(1)***

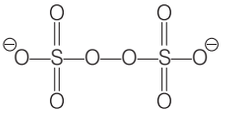
Only S_2-form of sulphur is paramagnetic in nature. Because S_2 is like O_2 i.e. paramagnetic as per molecular orbital theory. It contains unpaired electron. While α-sulphur and β-sulphur are diamagnetic as they do not have unpaired electron.

92 The number of bonds between sulphur and oxygen atoms in $S_2O_8^{2-}$ and the number of bonds between sulphur and sulphur atoms in rhombic sulphur, respectively, are **[2020, 8 Jan Shift-I]**

(a) 4 and 6 (b) 8 and 8
(c) 4 and 8 (d) 8 and 6

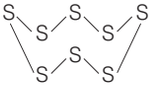
Ans. ***(b)***

$S_2O_8^{2-}$ is



Total number of S—O or S═O bond = 8

Rhombic sulphur is



Total number of S—S bond = 8

Thus, the correct answer is (b).

93 The acidic, basic and amphoteric oxides, respectively, are **[2020, 9 Jan Shift-I]**

(a) Cl_2O, CaO, P_4O_{10}
(b) N_2O_3, Li_2O, Al_2O_3
(c) Na_2O, SO_3, Al_2O_3
(d) MgO, Cl_2O, Al_2O_3

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Ans. ***(b)***

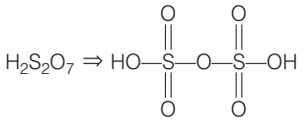
The acidic, basic and amphoteric oxides, respectively are N_2O_3, Li_2O and Al_2O_3. The normal oxides of the elements present on extreme left of periodic table are most acidic (Li_2O) as they form strong base when dissolved in water and oxides of the elements present in extreme right are acidic (N_2O_3). The amphoteric oxides show both the acidic and basic character (Al_2O_3).

94 The oxoacid of sulphur that does not contain bond between sulphur atoms is **[2019, 10 April Shift-I]**

(a) $H_2S_2O_3$ (b) $H_2S_2O_4$
(c) $H_2S_2O_7$ (d) $H_2S_4O_6$

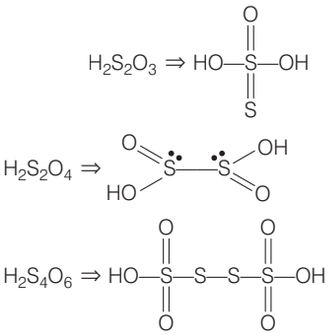
Ans. ***(c)***

S — S bond is not present in $H_2S_2O_7$ (pyrosulphuric acid or oleum).



While the other given oxoacids of sulphur, i.e.

$H_2S_2O_3$ (thiosulphuric acid), $H_2S_2O_4$ (hyposulphurous or dithionous acid) and $H_2S_4O_6$ (tetrathionic acid) contains S—S bonds.



95 When the first electron gain enthalpy ($\Delta_{e_g} H$) of oxygen is -141 kJ / mol, its second electron gain enthalpy is

(a) a positive value
(b) a more negative value than the first
(c) almost the same as that of the first
(d) negative, but less negative than the first **[2019, 9 Jan Shift-II]**

Ans. ***(a)***

As given, the first electron gain enthalpy of oxygen can be shown as,

$$O(g) + e^- \longrightarrow O^-(g), \quad \Delta_{e_g}H_1 = -141\ \text{kJ/mol}$$

The expression of second electron gain enthalpy of oxygen will be,

$$O^-(g) + e^- \longrightarrow O^{2-}(g), \quad \Delta_{e_g}H_2 = +\text{ve}$$

$\Delta_{e_g}H_2$ of oxygen is positive, i.e. endothermic, because a strong electrostatic repulsion will be observed between highy negative O^- and the incoming electron (e^-). A very high amount of energy will be consumed (endothermic) by the system to overcome the electrostatic repulsion.

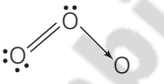
96 Which of the following is wrong statement?

(a) ONCl and ONO^- are not isoelectronic
(b) O_3 molecule is bent
(c) Ozone is violet-black in solid sate
(d) Ozone is diamagnetic gas **[JEE Main 2013]**

Ans. ***(*)***

(a) Number of electrons in
ONCl = 3.2 e^-; ONO^- = 24 e^-
Thus, ONCl and ONO^- are not isoelectronic.

(b) O_3 has bent shape structure.
Central atom O is sp^2 hybridised with 1 lone pair of electrons.



(c) Ozone is violet-black in solid state.
(d) O_3 has no unpaired electrons, thus it is diamagnetic.
Hence, all the given statements are correct.

97 Which of the following statements regarding sulphur is incorrect? **[AIEEE 2011]**

(a) S_2 molecule is paramagnetic
(b) The vapour at 200°C consists mostly of S_8 rings
(c) At 600°C, the gas mainly consists of S_2 molecules
(d) The oxidation state of sulphur is never less than +4 in its compounds

Ans. ***(d)***

(a) S_2 molecule is paramagnetic due to unpaired electrons in *MO* and is blue coloured compound, thus true.
(b) The vapour at 200°C consists mostly of S_8 rings, thus correct.
(c) At 600°C, the gas mainly consists of S_2 molecules, thus correct.
(d) Oxidation states of sulphur are

−2	in	H_2S
0	in	S_8
+2	in	$S_2O_3^{2-}$
+4	in	SO_2
+6	in	SO_3

Thus, incorrect. (Valency can be less than 4)

Hence, correct option is (d).

98 Which one of the following is an amphoteric oxide? **[AIEEE 2003]**

(a) ZnO (b) Na_2O
(c) SO_2 (d) B_2O_3

Ans. ***(a)***

ZnO can react with both acid as well as base to form salt and water.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

TOPIC 5
Group 17 Elements

99 Which one of the following correctly represents the order of stability of oxides, X_2O (X = halogen)? **[2021, 31 Aug Shift-II]**

(a) Br > Cl > I (b) Br > I > Cl
(c) Cl > I > Br (d) I > Cl > Br

Ans. ***(d)***

Iodine oxygen bond is stable due to greater polarity of bond. Stability of chlorine oxygen bond is due to multiple bond formation of oxygen with *d*-orbital of chlorine atom.

Bromine lacks both these characteristics. So, the stability order of oxide is I > Cl > Br.

100 The number of halogen (s) forming halic (V) acid is **[2021, 31 Aug Shift-I]**

Ans. ***(3)***

The halic (V) acids formed by chlorine (Cl), bromine (Br) and iodine (I) are $HClO_3$, $HBrO_3$ and HIO_3 respectively.

101 Which one of the following is used to remove most of plutonium from spent nuclear fuel? **[2021, 27 Aug Shift-II]**

(a) ClF_3 (b) O_2F_2 (c) I_2O_5 (d) BrO_3

Ans. ***(b)***

Dioxygen difluoride is used to remove the plutonium from spent nuclear fuel.

$$3F-O-O-F + \underset{\text{(From nuclear fuel)}}{Pu} \longrightarrow PuF_6 + 3O_2\uparrow$$

Therefore, the option (b) is correct.

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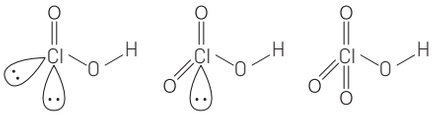
102 Number of Cl═O bonds in chlorous acid, chloric acid and perchloric acid respectively are

[2021, 27 July Shift-II]

(a) 3, 1 and 1 (b) 4, 1 and 0
(c) 1, 1 and 3 (d) 1, 2 and 3

Ans. ***(d)***

Structure of chlorous acid, chloric acid and perchloric acid are shown below



Chlorous acid Chloric acid Perchloric acid

Formula	$HClO_2$	$HClO_3$	$HClO_4$
No. of Cl═O	1	2	3

103 Choose the incorrect statement.

[2021, 26 Aug Shift-I]

(a) Cl_2 is more reactive than ClF.
(b) F_2 is more reactive than ClF.
(c) On hydrolysis ClF froms HOCl and HF.
(d) F_2 is a stronger oxidising agent than Cl_2 in aqueous solution.

Ans. ***(a)***

The Cl_2 is more reactive than ClF is incorrect statement as reactivity order can be written as follows

F_2 > ClF (interhalogen compounds) > Cl_2.

Interhalogen compounds are more reactive than pure halogen compounds as the bonds are polar and weaker than pure halogen compounds.

∴ statement (a) is incorrect.

F_2 is highly reactive among all interhalogens or pure halogen compounds due to strong interelectronic repulsion between F-atoms.

104 The absolute value of the electron gain enthalpy of halogens satisfies

[2021, 17 March Shift-I]

(a) I > Br > Cl > F (b) Cl > Br > F > I
(c) Cl > F > Br > I (d) F > Cl > Br > I

Ans. ***(c)***

Order of electron gain enthalpy (absolute value)

Cl > F > Br > I

Element	F	Cl	Br	I
ΔH_{eg} (kJ/mol)	−328	−349	−325	−295

Absolute value of electron gain enthalpy decreases down the group in a periodic table due to increase in size.

But magnitude of electron gain enthalpy of second period element F is slightly less than third period element 'Cl' owing to its small size. Due to small size of 'F' there is high electronic repulsion between the existing and approaching electron.

Hence, magnitude of electron gain enthalpy decreases.

105 The correct order of bond dissociation enthalpy of halogens is

[2021, 25 Feb Shift-II]

(a) $F_2 > Cl_2 > Br_2 > I_2$
(b) $I_2 > Br_2 > Cl_2 > F_2$
(c) $Cl_2 > Br_2 > F_2 > I_2$
(d) $Cl_2 > F_2 > Br_2 > I_2$

Ans. ***(c)***

Among halogens (F_2, Cl_2, Br_2 and I_2), bond dissociation enthalpy ($\Delta_{diss}H°$) of I_2, is minimum because of larger size of I-atom there is a steric repulsion between bonded I-atoms, which makes I—I bond weakest.

Whereas, smaller size and highest electronegativity of F-atom cause highest electron density on F-atom of F_2 molecule.

As a result, F—F bond becomes weaker due to electrostatic repulsion between bonded F-atoms.

Thus, the order of $\Delta_{diss}H°$ (in kJ mol^{-1}) is

Cl—Cl (242.6) > Br—Br (192.3) > F—F (158.8) > I—I (151.1)

F—F: Electrostatic repulsion; I—I: Steric repulsion

106 Among the following, the number of halide(s) which is/are inert to hydrolysis is ..... .

[2021, 25 Feb Shift-I]

(i) BF_3 (ii) $SiCl_4$
(iii) PCl_5 (iv) SF_6

Ans. ***(1)***

BF_3, $SiCl_4$ and PCl_5 are easily hydrolysed while SF_6 is inert to hydrolysis due to the presence of sterically protected sulphur atom by six F atoms, which does not permit the reactions like hydrolysis to take place.

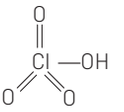
Thus, only 1 halide is inert to hydrolysis.

107 The number of Cl ═ O bonds in perchloric acid is ".....".

[2020, 6 Sep Shift-I]

Ans. ***(3.00)***

Perchloric acid is $HClO_4$. Structure of $HClO_4$ is



Thus, Cl═O bond is 3.

Hence, the correct answer is 3.

108 Chlorine reacts with hot and concentrated NaOH and produces compounds (*X*) and (*Y*). Compound (*X*) gives white precipitate with silver nitrate solution. The average bond order between Cl and O atoms in (*Y*) is ..... .

[2020, 7 Jan Shift-I]

Ans. ***(1.67)***

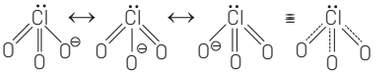
The reaction is,

$3Cl_2 + 6NaOH \longrightarrow \underset{(X)}{5NaCl} + \underset{(Y)}{NaClO_3} + 3H_2O$

$(X) \xrightarrow{+AgNO_3}$ AgCl (white ppt.)

Y = $NaClO_3$ (Na^+ and ClO_3^-)

The structure of ClO_3^- (chlorate ion) is,



'Cl—O' bond order in the hybrid

$$= \frac{\text{Number of bonds between Cl and O}}{\text{Total number of O (surrounding atoms)}}$$

$$= \frac{5}{3} = 1.66 \text{ or } 1.67$$

109 Among the following reactions of hydrogen with halogens, the one that requires a catalyst is

(a) $H_2 + Cl_2 \longrightarrow 2HCl$
(b) $H_2 + I_2 \longrightarrow 2HI$
(c) $H_2 + F_2 \longrightarrow 2HF$
(d) $H_2 + Br_2 \longrightarrow 2HBr$

[2019, 10 Jan Shift-II]

Ans. ***(b)***

Chemical reactivity of halogens decreases down the group.

The chemical reactivity follows the order.

∴ $F_2 > Cl_2 > Br_2 > I_2$.

The highest reactivity of fluorine is attributed to two factors :

(i) The low dissociation energy of F—F bond (which results in low attraction energy for the reaction).
(ii) Very strong bonds which are formed.

Both properties arise from, small size of fluorine. I_2 is being the least

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reactive halogen, it requires a catalyst for the reaction.

$$H_2 + I_2 \longrightarrow 2HI$$

110 What products are expected from the disproportionation reaction of hypochlorous acid ? **[AIEEE 2006]**

(a) $HClO_3$ and Cl_2O
(b) $HClO_2$ and $HClO_4$
(c) HCl and Cl_2O
(d) HCl and $HClO_3$

Ans. ***(d)***

$$3HOCl \longrightarrow 2HCl + HClO_3$$

111 The correct statement about ICl_5 and ICl_4^- is **[2019, 8 April Shift II]**

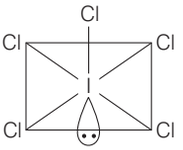
(a) ICl_5 is square pyramidal and ICl_4^- is tetrahedral
(b) ICl_5 is square pyramidal and ICl_4^- is square planar
(c) Both are isostructural
(d) ICl_5 is trigonal bipyramidal and ICl_4^- is tetrahedral

Ans. ***(b)***

For $\ddot{I}Cl_5$

$$H = \frac{1}{2}(7 + 5 - 0 + 0) = 6\,(sp^3d^2)$$

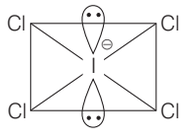
[refer the solution of Q. No. 4]



sp^3d^2-hybridised
Geometry : Octahedral
Shape / Structure : Square pyramidal

For $\ddot{I}Cl_4^-$

$$H = \frac{1}{2}(7 + 4 - 0 + 1) = 6\,(sp^3d^2)$$



sp^3d^2-hybridised
Geometry : Octahedral
Shape/Structure : Square planar

So, ICl_5 and ICl_4^- are isolobal but not isostructural.

112 HF has highest boiling point among hydrogen halides, because it has **[2019, 10 April Shift-I]**

(a) lowest ionic character
(b) strongest van der Waals' interactions
(c) strongest hydrogen bonding
(d) lowest dissociation enthalpy

Ans. ***(c)***

HF has highest boiling point among hydrogen halides because it has strongest hydrogen bonding. Here, the hydrogen bond exists between hydrogen of one molecule and fluorine atom of another molecule as shown below.

$$\overset{\delta+}{H}\text{—}\overset{\delta-}{F}\ldots\overset{\delta+}{H}\text{—}\overset{\delta-}{F}\ldots\overset{\delta+}{H}\text{—}\overset{\delta-}{F}$$

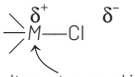
In this molecule, hydrogen bond behaves like a bridge between two atoms that holds one atom by covalent bond and the other by hydrogen bond.

113 The chloride that cannot get hydrolysed is **[2019, 11 Jan Shift-I]**

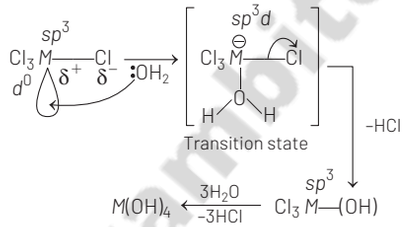
(a) $SnCl_4$ (b) CCl_4
(c) $PbCl_4$ (d) $SiCl_4$

Ans. ***(b)***

The compounds given are the tetrahalides (MCl_4) of group 14 elements. For the hydrolysis, (nucleophilic substitution) of MCl_4 the nature of the M—Cl bond should be as:



It must expand its covalency beyond 4 by the use of its vacant d-orbital which will accommodate the lone pair of electrons of H_2O (the-nucleophile).



Here, M can be Si, Sn and Pb because they have vacant *nd*-orbital. But, carbon is a member of second period ($n = 2, l = 0, 1$), it does not have *d*-orbital ($l = 2$). So, CCl_4 will not be hydrolysed and correct option is (b).

114 Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y, is **[2019, 12 Jan Shift-I]**

(a) 1 (b) 3
(c) 7 (d) 5

Ans. ***(d)***

Iodine reacts with concentrated HNO_3 to yield HIO_3 along with NO_2 and H_2O. The reaction involved in as follows :

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

The oxidation state of 'I' in HIO_3 is + 5 as calculated below :

$$1 + x + 3(-2) = 0$$
$$x - 5 = 0$$
$$x = +5$$

115 Chlorine on reaction with hot and oncentrated sodium hydroxide gives **[2019, 12 Jan Shift-II]**

(a) Cl^- and ClO^- (b) Cl^- and ClO_3^-
(c) ClO_3^- and ClO_2^- (d) Cl^- and ClO_2^-

Ans. ***(b)***

Halogens form halates and halides with hot and concentrated solution of NaOH as :

$$3X_2 + 6NaOH \longrightarrow 5NaX + NaXO_3 + 3H_2O$$

So, Cl_2 will also give Cl^- (as NaCl) and ClO_3^- (as $NaClO_3$) in the above reaction.

Thus, option (b) is correct.

Note When halogens react with cold and dilute solution of NaOH, hypohalites and halides are produced as:

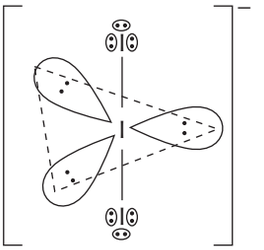
$$X_2 + 2NaOH \longrightarrow NaX + NaXO + H_2O$$

116 Total number of lone pair of electron in I_3^- ion is **[JEE Main 2018]**

(a) 3 (b) 6 (c) 9 (d) 12

Ans. ***(c)***

The structure of I_3^- ion is



Hence, 9 is the correct answer.

117 The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are **[JEE Main 2017]**

(a) ClO^- and ClO_3^- (b) ClO_2^- and ClO_3^-
(c) Cl^- and ClO^- (d) Cl^- and ClO_2^-

Ans. ***(c)***

Cl_2, Br_2 and I_2 form a mixture of halide and hypohalites when react with cold dilute alkalies while a mixture of halides and haloate when react with concentrated cold alkalies.

$$Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$$

(Cold and dilute)

$\therefore$ Cl^- and ClO^- are obtained as products when chlorine gas reacts with cold and dilute aqueous NaOH.

118 Which among the following is the most reactive? **[JEE Main 2015]**

(a) Cl_2 (b) Br_2 (c) I_2 (d) ICl

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Ans. ***(d)***

Cl_2, Br_2 and I_2 are homonuclear diatomic molecule in which electronegativity of the combining atoms is same, so they are more stable and less reactive, whereas, I and Cl have different electronegativities and bond between them are polarised and hence, reactive. Therefore, interhalogen compounds are more reactive.

Time Saving Technique *In this type of question of halogen, only go through the polarity of the molecule. As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.*

119 Among the following oxoacids, the correct decreasing order of acid strength is

(a) $HOCl > HClO_2 > HClO_3 > HClO_4$
(b) $HClO_4 > HOCl > HClO_2 > HClO_3$
(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$
(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

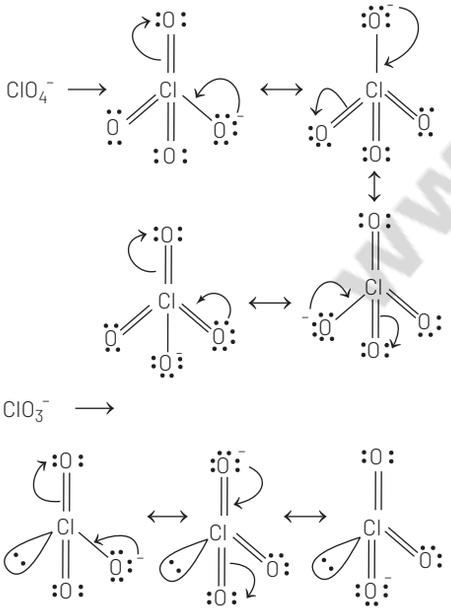
[JEE Main 2014]

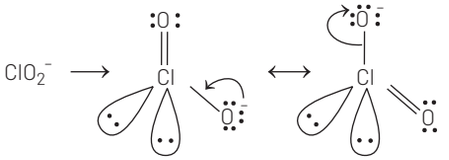
Ans. ***(c)***

Acidic strength of oxoacids depends upon the stability of conjugate base. More stable the conjugate base of an acid, stronger is the acid.

$$HClO_4 \rightleftharpoons ClO_4^- + H^+$$
$$HClO_3 \rightleftharpoons ClO_3^- + H^+$$
$$HClO_2 \rightleftharpoons ClO_2^- + H^+$$
$$HOCl \rightleftharpoons ClO^- + H^+$$

Conjugate bases stabilizes by resonance.





ClO^- does not show resonance. Thus, the stability order of conjugate base due to resonance is

$$ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$$

Hence, the acidic strength of given oxoacids is as follows

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

120 Identify the incorrect statement among the following **[AIEEE 2007]**

(a) Ozone reacts with SO_2 to give SO_3
(b) Silicon reacts with NaOH (*aq*) in the presence of air to give Na_2SiO_3 and H_2O
(c) Cl_2 reacts with excess of NH_3 to give N_2 and HCl
(d) Br_2 reacts with hot and strong NaOH solution to give NaBr, $NaBrO_4$ and H_2O

Ans. ***(d)***

Br_2 reacts with hot and strong NaOH to give NaBr, $NaBrO_3$ and H_2O.

121 A metal, *M* forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? **[AIEEE 2006]**

(a) MCl_2 is more volatile than MCl_4
(b) MCl_2 is more soluble in anhydrous ethanol than MCl_4
(c) MCl_2 is more ionic than MCl_4
(d) MCl_2 is more easily hydrolysed than MCl_4

Ans. ***(c)***

In MCl_2, oxidation state of $M = +2$

In MCl_4, oxidation state of $M = +4$

Higher the oxidation state, smaller is the size.

Greater the polarising power, greater is the covalent characteristic.

Hence, MCl_4 is more covalent and MCl_2 is more ionic

122 The correct order of the thermal stability of hydrogen halides (H—X) is **[AIEEE 2005]**

(a) HI > HCl > HF > HBr
(b) HCl < HF > HBr < HI
(c) HF > HCl > HBr > HI
(d) HI > HBr > HCl > HF

Ans. ***(c)***

In a group, $\Delta G°_f$ (HX) changes from negative to positive downwards.

$HF(g)$, $\Delta G = -273.20$ kJ mol^{-1}

$HI(g)$, $\Delta G = +1.72$ kJ mol^{-1}

Thus, HF is thermally stable and HI not.

Thus, HF > HCl > HBr > HI

123 Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. The explanation for it is that

(a) concentrated hydrochloric acid emits strongly smelling HCl gas all the time
(b) oxygen in air reacts with the emitted HCl gas to form a cloud of chlorine gas
(c) strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke
(d) due to strong affinity for water, concentrated hydrochloric acid pulls moisture of air towards itself. This moisture forms droplets of water and hence, the cloud **[AIEEE 2003]**

Ans. ***(b)***

$$2HCl + \frac{1}{2}O_2 \longrightarrow H_2O + Cl_2$$

TOPIC 6
Group 18 Elements

124 Match List-I with List-II.

	List-I (Species)		**List-II** (Number of lone pair of electrons on the central atom)
A.	XeF_2	1.	0
B.	XeO_2F_2	2.	1
C.	XeO_3F_2	3.	2
D.	XeF_4	4.	3

Choose the most appropriate answer from the options given below : **[2021, 27 Aug Shift-I]**

	A	B	C	D
(a)	4	1	2	3
(b)	3	4	2	1
(c)	3	2	4	1
(d)	4	2	1	3

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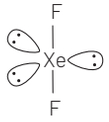
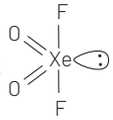
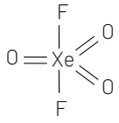
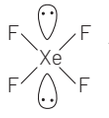
Ans. ***(d)***

The geometries of

A. XeF_2  Three lone pairs

B. XeO_2F_2  One lone pair

C. XeO_3F_2  Zero lone pair

D. XeF_4  Two lone pairs

So, the correct match is A-4, B-2, C-1, D-3.

125 A xenon compound '*A*' upon partial hydrolysis gives XeO_2F_2. The number of lone pair of electrons present in compound *A* is ..... (Round off to the nearest integer).

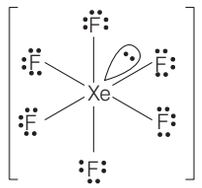
[2021, 18 March Shift-II]

Ans. ***(19)***

Xenon hexa fluoride (*A*) on partial hydrolysis gives XeO_2F_2 as a product.

$$\underset{\substack{(A)\\ \text{Xenon hexa fluoride}}}{XeF_6} + \underset{\text{Partially}}{2H_2O} \longrightarrow XeO_2F_2 + 4HF$$

Structure of XeF_6



$\therefore$ Total no. of lone pair = lone pair on Xe + 6 × lone pair on F = 1 + 6 × 3 = 19

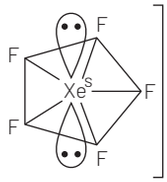
126 The shape/structure of $[XeF_5]^-$ and XeO_3F_2, respectively, are

[2020, 2 Sep Shift-II]

(a) pentagonal planar and trigonal bipyramidal
(b) octahedral and square pyramidal
(c) trigonal bipyramidal and pentagonal planar
(d) trigonal bipyramidal and trigonal bipyramidal

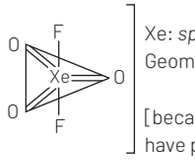
Ans. ***(a)***

$[XeF_5]^-$



Xe : sp^3d^3-hybridised
Geometry = Pentagonal bipyramidal
Shape/Structure = Pentagonal planar

XeO_3F_2



Xe: sp^3d-hybridised
Geometry = Shape/ structure = Trigonal bipyramidal
[because, Xe in XeO_3F_2 does not have pair of electrons]

127 The reaction in which the hybridisation of the underlined atom is affected is

[2020, 4 Sep Shift-II]

(a) $\underline{Xe}F_4 + SbF_5 \longrightarrow$

(b) $H_2\underline{S}O_4 + NaCl \xrightarrow{420\ K}$

(c) $H_3\underline{P}O_2 \xrightarrow{\text{Disproportionation}}$

(d) $\underline{N}H_3 \xrightarrow{H^+}$

Ans. ***(a)***

Complete reaction with change in hybridisation is as follows :

(a) $\underset{sp^3d^2}{\underline{Xe}F_4} + SbF_5 \longrightarrow \underset{sp^3d}{[XeF_3]^+}[SbF_6]^-$

Change in hybridisation

(b) $H_2\underset{sp^3}{\underline{S}}O_4 + 2NaCl \longrightarrow Na_2\underset{sp^3}{SO_4} + 2HCl$

No change in hybridisation

(c) $H_3PO_2 \xrightarrow[\Delta]{\text{Disproportionation}} \underset{sp^3}{H_3PO_4} + \underset{sp^3}{PH_3}$

No change in hybridisation

(d) $\underset{sp^3}{\ddot{N}H_3} \xrightarrow{N^+} \underset{sp^3}{\overset{+}{N}H_4}$

No change in hybridisation

In the reaction (a), hybridisation of Xe in XeF_4 is sp^3d^2 converted into $[XeF_3]^+$ and hybridisation of Xe in $[XeF_3]^+$ is sp^3d.

In this reaction, sp^3d^2-hybridisation change into sp^3d.

128 The type of hybridisation and number of lone pair(s) of electrons of Xe in $XeOF_4$, respectively, are

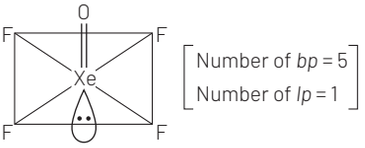
[2019, 10 Jan Shift-I]

(a) sp^3d^2 and 1 (b) sp^3d and 2
(c) sp^3d and 1 (d) sp^3d^2 and 2

Ans. ***(a)***

In $XeOF_4$, Xe is sp^3d^2-hybridised. Geometry of the molecule is octahedral, but shape of the molecule is square pyramidal.

According to VSEPR, theory it has one π bond. Remaining six electron pairs form an octahedron with one position occupied by a lone pair.



Number of *bp* = 5
Number of *lp* = 1

Here, Xe contains one lone pair of electrons.

129 The noble gas that does not occur in the atmosphere is

[2019, 10 April Shift-II]

(a) Ra (b) Kr (c) He (d) Ne

Ans. ***(a)***

Radium (Ra) is a radioactive element. Ra belongs to group 2 (alkaline earth metals), it is not a noble gas.

Note In question noble gas which does not exist in the atmosphere is asked and answer is Ra. But Ra (radium) is an alkaline earth metal and not noble gas. It can be Rn (radon) and is misprint in JEE Main Paper.

130 Which one has the highest boiling point? **[JEE Main 2015]**

(a) He (b) Ne (c) Kr (d) Xe

Ans. ***(d)***

As we move down the group of noble gases, molecular mass increases by which dipole produced for a moment and hence London forces increases from He to Xe. Therefore more amount of energy is required to break these forces, thus boiling point also increases from He to Xe.

131 Which one of the following reaction of xenon compounds is not feasible? **[AIEEE 2009]**

(a) $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$
(b) $3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$
(c) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
(d) $XeF_6 + RbF \longrightarrow Rb[XeF_7]$

Ans. ***(a)***

XeF_6 has much tendency to hydrolyse. The reverse reaction is more spontaneous.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

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18

d and *f*-Block Elements

TOPIC 1

Characteristics of *d*-block Elements

01 The nature of oxides V_2O_3 and CrO is indexed as '*X*' and '*Y*' type respectively. The correct set of *X* and *Y* is **[2021, 27 Aug Shift-I]**

(a) *X* = basic, *Y* = amphoteric
(b) *X* = amphoteric, *Y* = basic
(c) *X* = acidic, *Y* = acidic
(d) *X* = basic, *Y* = basic

Ans. ***(d)***

V_2O_3 is a basic oxide as on dissolving in acids, give solution of vanadium (III) complexes. In case of transition metal oxide, the metal with lower oxidation states are basic. So, CrO is also basic as oxidation state of Cr is +2.

02 Which one of the following when dissolved in water gives coloured solution in nitrogen atmosphere? **[2021, 26 Aug Shift-I]**

(a) $CuCl_2$ (b) AgCl (c) $ZnCl_2$ (d) Cu_2Cl_2

Ans. ***(a)***

$CuCl_2$ will dissolve in water to give blue colour Cu^{2+} ions. The colour is due to the presence of unpaired e^- in Cu^{2+} ions.

$$CuCl_2 + nH_2O \longrightarrow \underset{\text{(Blue colour)}}{Cu^{2+}(aq)}$$

AgCl and Cu_2Cl_2 are insoluble in water while $ZnCl_2$ on dissolving in water forms colourless solution due to formation of Zn^{2+} ions, which has no unpaired e^-.

03 The spin only magnetic moments (in BM) for free Ti^{3+}, V^{2+}, and Sc^{3+} ions respectively are
(Atomic number: Sc = 21, Ti = 22, V = 23) **[2021, 25 July Shift-II]**

(a) 3.87, 1.73, 0 (b) 1.73, 3.87, 0
(c) 1.73, 0, 3.87 (d) 0, 3.87, 1.73

Ans. ***(b)***

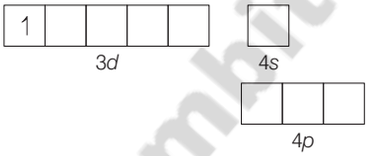
Spin magnetic moment is a magnetic moment caused due to the spin of particles.

The formula to find the spin only magnetic moment is,

$$\mu = \sqrt{n(n+2)}$$

where, n = number of unpaired electrons

$Ti^{3+}(22) \rightarrow [Ar]\,3d^1$

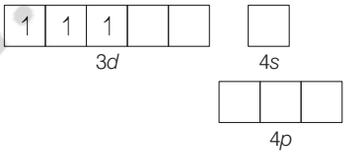


Only 1 unpaired electron.

$\therefore \quad n = 1$

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73\ \text{BM}$$

$V^{2+}(23) \rightarrow [Ar]\,3d^3$

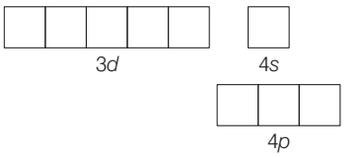


3 unpaired electrons.

$\therefore \quad n = 3$

$$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87\ \text{BM}$$

$Sc^{3+}(21) \rightarrow [Ar]\,3d^0 4s^0$



No electron, $n = 0$

$\therefore \quad \mu = \sqrt{0(0+2)} = 0$

04 In the ground state of atomic Fe(Z = 26), the spin-only magnetic moment is ..... $\times 10^{-1}$ BM. (Round off to the nearest integer).
[Given : $\sqrt{3} = 1.73, \sqrt{2} = 1.41$] **[2021, 17 March Shift-II]**

Ans. ***(49)***

Electronic configuration of Fe : $1s^2\ 2s^2\ 2p^6\ 3s^2$

In $3d^6$, number of unpaired electrons (n) = 4

Spin only magnetic moment

$$= \sqrt{n(n+2)}\ \text{BM}$$
$$= \sqrt{4(4+2)}$$
$$= \sqrt{24} = 4.9$$
$$= 49 \times 10^{-1}$$

Nearest integer value will be 49.

05 The common positive oxidation states for an element with atomic number 24, are **[2021, 17 March Shift-II]**

(a) +2 to +6
(b) +1 and +3 to +6
(c) +1 and +3
(d) +1 to +6

Ans. ***(a)***

Common positive oxidation states for an element with atomic number 24, are +2 to +6.

Chromium (Z = 24)

Electronic configuration: $[Ar]\,4s^1\,3d^5$

It has five electrons in 3*d*-subshell and one electron in 4*s* -subshell. Thus, chromium metal has six valence electrons. Chromium can lose some or all of its valence electrons to form ions with different oxidation states. Thus, chromium shows the oxidation states of +1, +2, +3, +4, +5 and +6 respectively.

The most common oxidation states of chromium are +2, +3 and +6.

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06 The major components of German silver are **[2021, 25 Feb Shift-II]**

(a) Cu, Zn and Ag
(b) Cu, Zn and Ni
(c) Ge, Cu and Ag
(d) Zn, Ni and Ag

Ans. ***(b)***

The major components of German silver are Cu : 25-30%, Zn : 25-30% and Ni : 40-30%.

07 In which of the following pairs, the outer most electronic configuration will be the same? **[2021, 25 Feb Shift-I]**

(a) V^{2+} and Cr^{+} (b) Cr^{+} and Mn^{2+}
(c) Ni^{2+} and Cu^{+} (d) Fe^{2+} and Co^{+}

Ans. ***(b)***

(a) V^{2+} -$[Ar]3d^3$; Cr^{+} -$[Ar]3d^5$
(b) Cr^{+} -$[Ar]3d^5$; Mn^{2+} -$[Ar]3d^5$
(c) Ni^{2+} -$[Ar]3d^8$; Cu^{+} -$[Ar]3d^{10}$
(d) Fe^{2+} -$[Ar]3d^6$; Co^{+} -$[Ar]3d^7 4s^1$

Thus, in option (b), both ions have same outer most electronic configuration.

08 The incorrect statement among the following is **[2021, 24 Feb Shift-II]**

(a) $VOSO_4$ is a reducing agent.
(b) Cr_2O_3 is an amphoteric oxide.
(c) RuO_4 is an oxidising agent.
(d) Red colour of ruby is due to the presence of Co^{3+}.

Ans. ***(d)***

Red colour of ruby is due to presence of Cr^{3+} ions in Al_2O_3. Chromium is the trace element that causes ruby's red colour, which ranges from an orange red to a publish re(d) The strength of ruby's red depends on how much chromium is present.

09 What is the correct order of the following elements with respect to their density ? **[2021, 24 Feb Shift-II]**

(a) Cr < Zn < Co < Cu < Fe
(b) Zn < Cu < Co < Fe < Cr
(c) Zn < Cr < Fe < Co < Cu
(d) Cr < Fe < Co < Cu < Zn

Ans. ***(c)***

Generally, due to decrease in metallic radius and increase in atomic mass density increase across the period from left to right.

Metal	**Density** (g/cm^3)
Zn	7.13
Cr	7.19
Fe	7.8
Co	8.7
Cu	8.9

Correct order is

Cu > Co > Fe > Cr > Zn.

10 Given below are two statements.

Statement I Colourless cupric metaborate is reduced to cuprous metaborate in a luminous flame.

Statement II Cuprous metaborate is obtained by heating boric anhydride and copper sulphate in a non-luminous flame.

In the light of the above statements, choose the most appropriate answer from the options given below. **[2021, 24 Feb Shift-I]**

(a) Both statement I and statement II are true.
(b) Both statement I and statement II are false.
(c) Statement I is true but statement II is false.
(d) Statement I is false but statement II is true.

Ans. ***(b)***

(i) In presence of luminous flame, blue cupric metaborate is reduced to colourless cuprous metaborate.

$$2Cu(BO_2)_2 + 2NaBO_2 + C \xrightarrow[\text{flame}]{\text{Luminous}} 2CuBO_2 + Na_2B_4O_7 + CO$$

If non-luminous flame is present in reaction, cupric metaborate is obtained by heating boric anhydride with copper sulphate.

$$CuSO_4 + B_2O_3 \xrightarrow[\text{flame}]{\text{Non-luminous}} \underset{\text{Cupric metaborate}}{Cu(BO)_2} + SO_3$$

11 The major components in Gun metal are **[2021, 24 Feb Shift-I]**

(a) Cu, Sn and Zn
(b) Cu, Zn and Ni
(c) Cu, Ni and Fe
(d) Al, Cu, Mg and Mn

Ans. ***(a)***

'Gun metal' also called as red brass (in USA). It is greyish in colour and originally used for making guns. The major components of 'Gun metal' are

Cu = 87%
Zn = 3%
Sn = 10%

It is also used in manufacturing of gears and bearing that are to be subjected to heavy loads and low speeds.

12 The electrode potential of M^{2+}/M of 3*d*-series elements shows positive value for **[2021, 24 Feb Shift-I]**

(a) Fe (b) Co
(c) Zn (d) Cu

Ans. ***(d)***

In the electrode potential series, only copper have positive value for electrode potential because copper has lower tendency than hydrogen to form ions. So, if standard hydrogen electrode ($E_{Cell} = 0$) is connected to copper half-cell, the copper with be relatively less negative or less number of electrons.

$E^{\circ}_{(Cu^{2+}/Cu)} = +0.34\,V;$
$E^{\circ}_{(Fe^{2+}/Fe)} = -0.41\ V$
$E^{\circ}_{Co^{+2}/Co} = -0.28\,V\ ;$
$E^{\circ}_{(Zn^{2+}/Zn)} = -0.76\,V$

∴ Electrode potential of Cu $E^{\circ}_{Cu^{+2}/Cu}$ show positive value.

13 The set that contains atomic numbers of only transition elements, is **[2020, 6 Sep Shift-I]**

(a) 37, 42, 50, 64
(b) 21, 25, 42, 72
(c) 9, 17, 34, 38
(d) 21, 32, 53, 64

Ans. ***(b)***

d-block elements in the periodic table are called transition elements. The set that contains atomic number of only transitive elements is 21, 25, 42, 72.

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					***d*-block**					
21	22	23	24	25	26	27	28	29	30	Sc (atomic no.) 21
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
39	40	41	42	43	44	45	46	47	48	Mn (atomic no.) 25
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
57	72	73	74	75	76	77	78	79	80	Mo (atomic no.) 42
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	
89	104	105	106	107	108	109	110	111	112	Hf (atomic no.) 72
Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uun	

Hence, the correct option is (b).

14 Consider the hydrated ions of Ti^{2+}, V^{2+}, Ti^{3+} and Sc^{3+}. The correct order of their spin-only magnetic moment is

[2019, 10 April Shift-I]

(a) $Sc^{3+} < Ti^{3+} < Ti^{2+} < V^{2+}$
(b) $Sc^{3+} < Ti^{3+} < V^{2+} < Ti^{2+}$
(c) $Ti^{3+} < Ti^{2+} < Sc^{3+} < V^{2+}$
(d) $V^{2+} < Ti^{2+} < Ti^{3+} < Sc^{3+}$

Ans. ***(a)***

The spin only magnetic moment (μ) of each ion can be calculated as :

$$\mu = \sqrt{n(n+2)}\ BM$$

[$\because n$ = No. of unpaired electron(s)]
$\Rightarrow \mu \propto n$, i.e. higher the number of unpaired electron, higher will be the value of μ.

Metal ion	Z	n (for metal ion)	M (BM)	Nature
Ti^{2+}	22	2 ($3d^2$)	$\sqrt{8}$	Paramagnetic
V^{2+}	23	3 ($3d^3$)	$\sqrt{15}$	Paramagnetic
Ti^{3+}	22	1 ($3d^1$)	$\sqrt{3}$	Paramagnetic
Sc^{3+}	21	0 ($3d^0$)	0	Diamagnetic

Thus, the correct order of spin only magnetic moments of given hydrated ions will be

$$Sc^{3+} < Ti^{3+} < Ti^{2+} < V^{2+}$$

15 The transition element having least enthalpy of atomisation is

(a) Zn (b) V
(c) Fe (d) Cu

[2019, 9 Jan Shift-II]

Ans. ***(a)***

For transition metals,

$\Delta H^{\circ}_{Atomisation} \propto$ Strength of metallic bonding

$\propto$ Number of unpaired electrons in the metal atom

For the given 3*d*-transition metals,

V	Fe	Cu	Zn
$3d^3 4s^2$	$3d^6 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^0$
$n=3$	$n=4$	$n=0$	$n=0$

[$\because n$ = no. of unpaired electrons]

$\Delta^{\circ} H_{Atomisation}$ (kJ mol^{-1})

= 515 418 339 130

So, absence of unpaired *d*-electrons and larger size of Zn atoms, make the crystal lattice of Zn less closely packed.

16 The highest value of the calculated spin only magnetic moment (in BM) among all the transition metal complexes is **[2019, 9 Jan Shift-I]**

(a) 5.92 (b) 3.87 (c) 6.93 (d) 4.90

Ans. ***(a)***

The spin only magnetic moment (μ) (in BM) is given by

$$\mu\ (\text{in BM}) = \sqrt{n(n+2)}$$

where, n = number of unpaired electrons
The highest value of n in transition metal complex is 5 in its d^5-configuration.

$$\therefore \quad \mu = \sqrt{5(5+2)}\ BM = 5.916\ BM$$

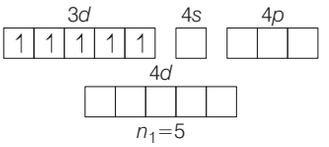
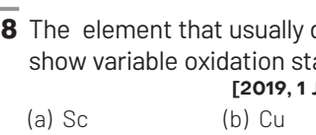
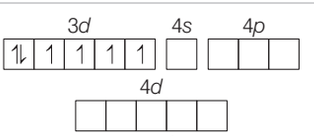
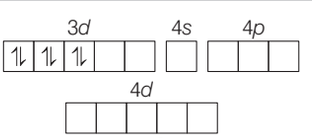
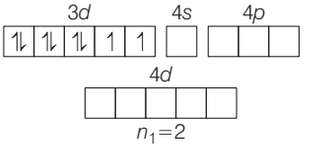
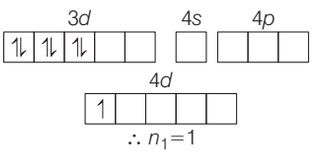
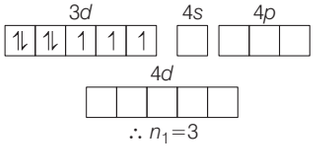
$$= 5.92\ BM$$

17 The difference in the number of unpaired electrons of a metal ion in its high-spin and low-spin octahedral complexes is two. The metal ion is **[2019, 10 Jan Shift-II]**

(a) Mn^{2+} (b) Fe^{2+}
(c) Ni^{2+} (d) Co^{2+}

Ans. ***(d)***

The difference in the number of unpaired electrons of different metal ions in their high spin and low spin octahedral complexes are given in the table below :

Metal ion	Number of e^- in high spin complex (n_1)	Number of e^- in low spin complex (n_2)	$n_2 - n_1$
Mn^{2+}	 $n_1=5$	 $n_2=1$	5 − 1 = 4
Fe^{2+}	 $n_1=4$	 $n_2=0$	4 − 0 = 4
Ni^{2+}	 $n_1=2$	 $\therefore n_1=1$	3 − 1 = 2
Co^{2+}	 $\therefore n_1=3$	Ni^{2+} does not form low spin octahedral complexes.	

18 The element that usually does not show variable oxidation states is

[2019, 1 Jan Shift-I]

(a) Sc (b) Cu
(c) Ti (d) V

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Ans. ***(a)***

The most stable oxidation states in the compounds of the given transition metals of 3*d*-series are,

Sc : +3; Ti : +3, +4; V : +2, +3, +4, +5; Cu : + 1, +2

The electronic configuration of Sc (Z = 21) is $[Ar]3d^1, 4s^2$.

Due to the presence of only one 3*d*-electron (no pairing energy) and two 4*s*-electrons, they easily ionise to achieve most stable +3 oxidation state.

19 The pair of metal ions that can given a spin-only magnetic moment of 3.9 BM for the complex $[M(H_2O)_6]Cl_2$, is

(a) Co^{2+} and Fe^{2+} (b) Cr^{2+} and Mn^{2+}
(c) V^{2+} and Co^{2+} (d) V^{2+} and Fe^{2+}

[2019, 12 Jan Shift-I]

Ans.*(c)*

As H_2O is a weak field ligan(d) It readily forms high spin complexes. In $[M(H_2O)_6]Cl_2$, M exist in +2 oxidation state. The arrangement of electrons in the given metal ions are as follows:

Metal ions	Configuration	Number of unpaired electrons	Spin only Magnetic moment (in BM) $= \sqrt{n(n+2)}$
Co^{2+}	$(d^7) = t_{2g}^5 e_g^2$	3	3.9
Fe^{2+}	$(d^6) = t_{2g}^4 e_g^2$	4	4.9
Cr^{2+}	$(d^4) = t_{2g}^3 e_g^1$	4	4.9
Mn^{2+}	$(d^5) = t_{2g}^3 e_g^2$	5	5.9
V^{2+}	$(d^3) = t_{2g}^3 e_g^0$	3	3.9

Therefore, Co^{2+} and V^{2+} contains same value of magnetic moment (3.9 BM).

20 The statement that is incorrect about the interstitial compounds is

[2019, 8 April Shift-II]

(a) they are very hard
(b) they have metallic conductivity
(c) they have high melting points
(d) they are chemically reactive

Ans. ***(d)***

Interstitial compounds are formed when a neutral atom with a small radius occupies in an interstitial hole (tetrahedral or octahedral voids) in a transition metal's hcp or ccp lattices (host lattice). Examples of small atoms (guest atom) are H, B, C and N.

Interstitial compounds are non-stoichiometric (Birtholide) in composition. They are very hard with very high melting points. The electrical conductivity of interstitial compounds are comparable to that of the pure metal. These are chemically unreactive in nature.

It is a hexadentate ligand.

21 The correct order of the first ionisation enthalpies is

[2019, 10 April Shift-II]

(a) Mn < Ti < Zn < Ni
(b) Ti < Mn < Zn < Ni
(c) Zn < Ni < Mn < Ti
(d) Ti < Mn < Ni < Zn

Ans. ***(d)***

The 3*d*-transition series is

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
		⇓			⇓			⇓	⇓	⇓
Outermost Electronic Configurection		$3d^2 4s^2$			$3d^5 4s^2$			$3d^8 4s^2$	$3d^{10} 4s^2$	

In 1st ionisation, one electron will be removed from $4s^2$ subshell/orbital.
With increase in atomic number (Z), i.e. with increase in number of protons in the nucleus, effective nuclear charge (Z^*) also increases from Sc to Zn.

$$IE \propto Z^*$$

So, IE order of the given elements will be,

Ti < Mn < Ni < Zn

22 The incorrect statement is

[2019, 10 April Shift-II]

(a) the gemstone, ruby, has Cr^{3+} ions occupying the octahedral sites of beryl
(b) the color of $[CoCl(NH_3)_5]^{2+}$ is violet as it absorbs the yellow light
(c) the spin only magnetic moments of $Fe(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ are nearly similar
(d) the spin only magnetic moment of $[Ni(NH_3)_4(H_2O)_2]^{2+}$ is 2.83 BM

Ans. ***(a)***

The explanation of given statements are as follows :

(a) Ruby, a pink or blood-red coloured gemstone belongs to corundum (Al_2O_3, alumina) system which has trigonal crystalline lattice containing the repeating unit of $Al_2O_3 - Cr^{3+}$. So, ruby does not belong to beryl lattice ($Be_3Al_2Si_6O_{18}$).
Thus, statement (a) is incorrect.

(b) $[Co(Cl)(NH_3)_5]^{2+}$ is a low spin octahedral complex of Co^{3+}. It absorbs low energy yellow light and high energy complementary violet light will be shown off. Thus, statement (b) is correct.

(c) $[Fe(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ are the high-spin octahedral complexes of Fe^{2+} ($3d^6$, $n = 4$) and Cr^{2+} ($3d^5$, $n = 5$) ions and weak field ligand, H_2O respectively. So, spin-only magnetic moment $= \sqrt{n(n+2)}$ of the complexes.

$[Fe(H_2O)_6]^{2+}$, $\mu_1 = \sqrt{4(4+2)}$
$(n = 4)$, $= \sqrt{24} = 4.89$ BM

$[Cr(H_2O)_6]^{2+}$, $\mu_2 = \sqrt{5(5+2)}$
$(n = 5)$, $= \sqrt{35} = 5.92$ BM

So, $\mu_1 \approx \mu_2$. Thus, statement (c) is correct.

(d) $[Ni(NH_3)_4(H_2O)_2]^{2+}$ is also a high-spin octahedral complex of Ni^{2+} ($3d^8$, $n = 2$)

$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ BM

Thus, statement (d) is correct.

23 The pair that has similar atomic radii is

[2019, 12 April Shift-II]

(a) Mn and Re (b) Ti and Hf
(c) Sc and Ni (d) Mo and W

Ans. ***(d)***

The pair that has similar atomic radii is Mo and W. It is due to lanthanoid contraction. The factor responsible for lanthanoid contraction is the imperfect shielding of one electron by another in the same set of orbitals. Shielding of 4*f* is very less due to its diffused shape. As a result, nuclear charge increases. Hence, Mo and W have similar atomic radii.

24 In the following reactions, ZnO is respectively acting as a/an

[JEE Main 2017]

(i) $ZnO + Na_2O \longrightarrow Na_2ZnO_2$
(ii) $ZnO + CO_2 \longrightarrow ZnCO_3$

(a) base and acid (b) base and base
(c) acid and acid (d) acid and base

Ans. ***(d)***

Zinc oxide (ZnO) when react with Na_2O it act as acid while with CO_2 it act as base. Therefore, it is an amphoteric oxide.

$$\underset{\text{Acid}}{ZnO} + \underset{\text{Base}}{Na_2O} \longrightarrow \underset{\text{Salt}}{Na_2ZnO_2}$$

$$\underset{\text{Base}}{ZnO} + \underset{\text{Acid}}{CO_2} \longrightarrow \underset{\text{Salt}}{ZnCO_3}$$

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25 Which of the following compounds is metallic and ferromagnetic? **[JEE Main 2016]**

(a) CrO_2 (b) VO_2
(c) MnO_2 (d) TiO_2

Ans. ***(a)***

Only three elements iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. CrO_2 is also a metallic and ferromagnetic compound which is used to make magnetic tapes for cassette recorders.

26 The reaction of zinc with dilute and concentrated nitric acid, respectively, produce **[JEE Main 2016]**

(a) NO_2 and NO (b) NO and N_2O
(c) NO_2 and N_2O (d) N_2O and NO_2

Ans. ***(d)***

$$Zn + \underset{(Conc.)}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

$$4Zn + \underset{(Dil.)}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

27 Which of the following arrangements does not represent the correct order of the property stated against it? **[JEE Main 2013]**

(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(d) Sc < Ti < Cr < Mn : number of oxidation states

Ans. ***(a)***

(a) V^{2+} = 3 unpaired electrons
Cr^{2+} = 4 unpaired electrons
Mn^{2+} = 5 unpaired electrons
Fe^{2+} = 4 unpaired electrons
Hence, the order of paramagnetic behaviour should be
$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(b) Ionic size decreases from left to right in the same period.

(c) (As per data from NCERT)
$Co^{3+} / Co^{2+} = 1.97$;
$Fe^{3+} / Fe^{2+} = 0.77$;
$Cr^{3+} / Cr^{2+} = -0.41$
Sc^{3+} is highly stable (It does not show + 2).

(d) The oxidation states increases as we go from group 3 to group 7 in the same period.

28 Four successive members of the first row transition elements listed below with atomic numbers. Which one of them is expected to have the highest $E^\circ_{M^{3+}/M^{2+}}$ value? **[JEE Main 2013]**

(a) Cr (Z = 24) (b) Mn (Z = 25)
(c) Fe (Z = 26) (d) Co (Z = 27)

Ans. ***(d)***

SRP value normally increases from left to right in the period of *d*-block elements. Some SRP value are exceptionally higher due to stability of product ion. *e.g.*,

$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.57$ V;

$E^\circ_{Co^{3+}/Co^{2+}} = +1.97$ V

Thus, $E^\circ_{M^{3+}/M^{2+}}$ is highest for Co.

29 The correct order of $E^\circ_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is **[AIEEE 2010]**

(a) Mn > Cr > Fe > Co
(b) Cr > Fe > Mn > Co
(c) Fe > Mn > Cr > Co
(d) Cr > Mn > Fe > Co

Ans. ***(a)***

Usually across the first transition series, the negative values for standard electrode potential decrease except for Mn due to stable d^5-configuration.

So, correct order : Mn > Cr > Fe > Co

30 In context with the transition elements, which of the following statements is incorrect?

(a) In addition to the normal oxidation state, the zero oxidation state is also shown by these elements in complexes **[AIEEE 2009]**

(b) In the highest oxidation states, the transition metal shows basic character and form cationic complexes

(c) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4*s* and 3*d* electrons are used for bonding

(d) Once the d^5 configuration is exceeded, the tendency to involve all the 3*d* electrons in bonding decreases

Ans. ***(b)***

As oxidation state increases, electronegativity increases thus acidic characteristic increases not basic

31 On heating, mixture of Cu_2O and Cu_2S will give **[AIEEE 2005]**

(a) Cu_2SO_3 (b) CuO + CuS
(c) $Cu + SO_3$ (d) $Cu + SO_2$

Ans. ***(d)***

Following reaction takes place during bessemerisation.

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

32 Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives **[AIEEE 2005]**

(a) HgO
(b) Hg_2O
(c) NH_2—Hg—HgCl
(d) $HgNH_2Cl$

Ans. ***(d)***

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{white}}{Hg(NH_2)Cl} + \underset{\text{black}}{Hg\downarrow} + NH_4Cl + 2H_2O$$

33 Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them ? **[AIEEE 2004]**

(a) $(n-1)d^8ns^2$ (b) $(n-1)d^5ns^1$
(c) $(n-1)d^3ns^2$ (d) $(n-1)d^5ns^2$

Ans. ***(d)***

$(n-1)d^8ns^2$ ⇅ ⇅ ⇅ 1 1 ⇅ 4(as in Ni)
($n-1$)d^8 ns^2

$(n-1)d^5ns^1$ 1 1 1 1 1 1 6(as in Cr)
($n-1$)d^5 ns^1

$(n-1)d^3ns^2$ 1 1 1 ⇅ 5(as in V)
($n-1$)d^3 ns^2

$(n-1)d^5ns^2$ 1 1 1 1 1 ⇅ 7(as in Mn)
($n-1$)d^5 ns^2

34 Which of the following groups of transition metals is called coinage metals? **[AIEEE 2003]**

(a) Cu, Ag, Au (b) Ru, Rh, Pd
(c) Fe, Co, Ni (d) Os, Ir, Pt

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Ans. ***(a)***

Cu, Ag, Au are called coinage metals because in the early times, they were used in making coins.

35 Which one of the following nitrates will leave behind a metal on strong heating? **[AIEEE 2003]**

(a) Ferric nitrate
(b) Copper nitrate
(c) Manganese nitrate
(d) Silver nitrate

Ans. ***(d)***

Metal oxides lying below Hg in electrochemical series decompose to form metal.

$$ZnO, MgO, CuO \xrightarrow{\Delta} \text{no effect}$$

$$Ag_2O \xrightarrow{\Delta} Ag + O_2$$

$$AgNO_3 \xrightarrow{\Delta} Ag_2O \longrightarrow Ag + O_2$$

36 For making good quality mirrors, plates of float glass are use(d) These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be **[AIEEE 2003]**

(a) mercury
(b) tin
(c) sodium
(d) magnesium

Ans. ***(a)***

Mercury (Hg) solidifies after glass, so used mercury for making good quality mirrors.

37 Which one of the following statements is correct? **[AIEEE 2003]**

(a) Manganese salts give a violet borax bead test in the reducing flame
(b) From a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl
(c) Ferric ions give a deep green precipitate on adding potassium ferrocyanide solution
(d) On boiling a solution having K^+, Ca^{2+} and HCO_3^- ions, we get a precipitate of $K_2Ca(CO_3)_2$

Ans. ***(b)***

Ammonia can dissolve precipitate of AgCl due to the formation of complex as given below

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2Cl]$$

38 A red solid is insoluble in water. However, it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is **[AIEEE 2003]**

(a) $(NH_4)_2Cr_2O_7$ (b) HgI_2
(c) HgO (d) Pb_3O_4

Ans. ***(b)***

HgI_2 becomes soluble in water, when KI is added to it due to the formation of $K_2Hg\,I_4$ complex which is soluble in water.

$$HgI_2 + 2KI \longrightarrow \underset{\text{(soluble)}}{K_2Hg\,I_4}$$

But when HgI_2 is heated, $Hg\,I_2$ decomposes to give violet coloured fumes of I_2 that deposits on the cooler parts of the test tube.

$$HgI_2 \xrightarrow{\Delta} Hg + I_2\uparrow$$

39 Which of the following ions has the maximum magnetic moment? **[AIEEE 2002]**

(a) Mn^{2+} (b) Fe^{2+}
(c) Ti^{2+} (d) Cr^{2+}

Ans. ***(a)***

Larger the number of unpaired electrons, greater the magnetic moment, $\mu = \sqrt{n(n+2)}$

where, n = Number of unpaired electrons

$Mn_{25} = [Ar]4s^2, 3d^5$

$Mn^{2+} = [Ar]3d^5 4s^0$

1	1	1	1	1

$3d^5$

Number of unpaired electrons = 5

$Fe_{26} = [Ar]4s^2, 3d^6$

$Fe^{2+} = [Ar]3d^6, 4s^0$

1↓	1	1	1	1

$3d^6$

Number of unpaired electrons = 4

$Ti_{22} = [Ar]4s^2 3d^2$

$Ti^{2+} = [Ar]3d^2 4s^0$

1	1			

$3d^2$

Number of unpaired electrons = 2

$Cr_{24} = [Ar]3d^5, 4s^1$

$Cr^{2+} = [Ar]3d^4, 4s^0$

1	1	1	1	

$3d^4$

Number of unpaired electrons = 4

Hence, Mn^{2+} : $[Ar]3d^5$ with five unpaired electrons have maximum magnetic moment.

TOPIC 2

Important Compounds of *d*-block Elements

40 In the given chemical reaction, colours of the Fe^{2+} and Fe^{3+} ions, are respectively

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

[2021, 1 Sep Shift-II]

(a) yellow, orange (b) yellow, green
(c) green, orange (d) green, yellow

Ans. ***(d)***

The Fe^{2+} ion has green colour while Fe^{3+} is yellow in colour.

41 In which one of the following sets all species show disproportionation reaction **[2021, 31 Aug Shift-II]**

(a) ClO_2^-, F_2, MnO_4^{2-} and $Cr_2O_7^{2-}$
(b) $Cr_2O_7^{2-}$, MnO_4^-, ClO_2^- and Cl_2
(c) ClO_2^-, Cl_2 and Mn^{3+}
(d) ClO_4^-, MnO_4^{2-}, ClO_2^- and F_2

Ans. ***(c)***

Disproportionation reactions are redox reaction in which a compound undergoes oxidation as well as reduction. The element of reacting species is in an intermediate oxidation state and simultaneously gets oxidised and reduced

$$\overset{+3}{3Cl}\,O_2^- \longrightarrow \overset{-1}{Cl}^- + 2\overset{+5}{Cl}\,O_3^-$$

$$\overset{0}{Cl}_2 + OH^- \longrightarrow \overset{-1}{Cl}^- + \overset{+5}{Cl}\,O_3^- + H_2O$$

$$2Mn^{3+} + 2H_2O \longrightarrow Mn^{2+} + \overset{+4}{Mn}\,O_2 + 4H^+$$

But MnO_4^- does not get disproportonated. Hence, option (c) is the correct answer.

42 Potassium permanganate on heating at 513 K gives a product which is **[2021, 27 Aug Shift-II]**

(a) paramagnetic and colourless
(b) diamagnetic and green

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(c) diamagnetic and colourless
(d) paramagnetic and green

Ans. ***(d)***

When $KMnO_4$ is heated at 513 K, it forms K_2MnO_4 and MnO_2 and O_2.

$$2K\overset{+7}{M}nO_4 \xrightarrow[513\,K]{D} K_2\overset{+6}{M}nO_4 + \underset{\text{(Black residue)}}{\overset{+4}{M}nO_2} + O_2$$
(Green)

$Mn_{25} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$

$Mn^{+6} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$;
1 unpaired electron, so paramagnetic

So, option (d) is correct.

43 The addition of dilute NaOH to Cr^{3+} salt solution will give **[2021, 27 Aug Shift-II]**

(a) a solution of $[Cr(OH)_4]^-$
(b) precipitate of $Cr_2O_3(H_2O)_n$
(c) precipitate of $[Cr(OH)_6]^{3-}$
(d) precipitate of $Cr(OH)_3$

Ans. ***(b)***

The addition of dil. NaOH to Cr^{3+} solution will produce ppt. of $Cr_2O_3(H_2O)_n$.

$$Cr^{3+} + NaOH \longrightarrow \underset{\text{(Precipitate)}}{Cr_2O_3(H_2O)_n}$$

Therefore, the option (b) is correct.

44 Which one of the following metals forms interstitial hydride easily ? **[2021, 25 July Shift-II]**

(a) Cr (b) Fe
(c) Mn (d) Co

Ans. ***(a)***

The metal like chromium (Cr) absorb dihydrogen in almost all stoichiometric quantities. This phenomenon is known as occlusion and compound formed are called as interstitial hydride or metallic hydride.

Elements of group 7, 8, 9 do not form hydrides. Only Cr will form hydride among the given elements (Fe, Mn, Co) (Mainly *d* and *f*-block elements form interstitial hydrides).

45 The correct order of following 3*d*-metal oxides, according to their oxidation numbers is

(A) CrO_3 (B) Fe_2O_3
(C) MnO_2 (D) V_2O_5
(E) Cu_2O **[2021, 25 July Shift-I]**

(a) (D) > (A) > (B) > (C) > (E)
(b) (A) > (C) > (D) > (B) > (E)
(c) (A) > (D) > (C) > (B) > (E)
(d) (C) > (A) > (D) > (E) > (B)

Ans. ***(c)***

Oxidation number of 3*d*-metal oxides are

A. $CrO_3 \rightarrow Cr \Rightarrow +6$
B. $Fe_2O_3 \rightarrow Fe \Rightarrow +3$
C. $MnO_2 \rightarrow Mn \Rightarrow +4$
D. $V_2O_5 \rightarrow V \Rightarrow +5$
E. $Cu_2O \rightarrow Cu \Rightarrow +1$

So, oxidation state order is

$CrO_3 > V_2O_5 > MnO_2 > Fe_2O_3 > Cu_2O$
or $A > D > C > B > E$.

46 The set having ions which are coloured and paramagnetic both is **[2021, 22 July Shift-II]**

(a) Cu^{2+}, Cr^{3+}, Sc^+
(b) $Cu^{2+}, Zn^{2+}, Mn^{4+}$
(c) Sc^{3+}, V^{5+}, Ti^{4+}
(d) $Ni^{2+}, Mn^{7+}, Hg^{2+}$

Ans. ***(a)***

Cu^{2+}, Cr^{3+} and Sc^+ are paramagnetic and coloured due to presence of unpaired electrons.

(i) Electronic configuration of
$_{29}Cu = [Ar]4s^1, 3d^{10}$
whereas for $Cu^{2+} = [Ar], 3d^9$
So, $n = 1$.

(ii) Electronic configuration of
$_{24}Cr = [Ar]4s^1, 3d^5$
whereas for $Cr^{3+} = [Ar], 3d^3$
So, $n = 3$.

(iii) Electronic configuration of
$_{21}Sc = [Ar]4s^2, 3d^1$
whereas for $Sc^+ = [Ar]4s^1, 3d^1$
So, $n = 2$.

Due to presence of unpaired electron(s) in Cu^{2+}, Cr^{3+} and Sc^+ they are paramagnetic and coloured.

Whereas
$Mn^{7+}(d^0), Hg^{2+}(d^{10}), Zn^{2+}(d^{10}), Cu^+(d^{10})$
$Sc^{3+}(d^0)$ and $Ti^{4+}(d^0)$ do not have unpaired electrons. So, they are colourless and diamagnetic in nature.

47 Number of electrons that vanadium ($Z = 23$) has in *p*-orbitals is equal to ..... . **[2021, 22 July Shift-II]**

Ans. ***(12)***

Vanadium ($Z = 23$)

Electronic configuration
$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

Total number of electrons in *p*-orbital is $6 + 6 = 12$.

48 The oxide that shows magnetic property is **[2021, 18 March Shift-II]**

(a) SiO_2 (b) Mn_3O_4 (c) Na_2O (d) MgO

Ans. ***(b)***

Generally, *d*-block elements shows magnetic property due to presence of unpaired electrons in its *d*-block. Mn i.e. manganese shows + 2 and +3 oxidation state.

Both having unpaired electrons as shown below

$_{25}Mn = [Ar]3d^5 4s^2$

$Mn^{2+}(3d^5 4s^0)$ having 5 unpaired electrons in 3*d* orbital.

$Mn^{+3}, (3d^4 4s^0)$ having 4 unpaired electrons in 3*d* orbital.

SiO_2, *p*-block element compound is commonly believed to be a typical diamagnetic as no unpaired electrons are present.

MgO and Na_2O also have unpaired electrons and hence are diamagnetic.

Hence, Mn_3O_4 show magnetic property.

49 FeX_2 and FeY_3 are known when *x* and *y* are **[2021, 16 March Shift-II]**

(a) *x* = F, Cl, Br, I and *y* = F, Cl and Br
(b) *x* = F, Cl, Br and *y* = F, Cl, Br and I
(c) *x* = Cl, Br, I and *y* = F, Cl, Br and I
(d) *x* = F, Cl, Br, I and *y* = F, Cl, Br and I

Ans. ***(a)***

FeI_3 does not exist because of I^-. Being a very good reducing agent, I^- reduces Fe^{3+} to Fe^{2+}.

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

Reducing nature order I > Br > Cl > F

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E° = 0.77\ V$$
$$I_2 + 2e^- \longrightarrow 2I^- \qquad E° = -0.54\ V$$

As standard reduction potential value of Fe^{3+} is more than I_2, so it is reduced to Fe^{2+}. Hence, except FeI_3, all other halogens can form iron halide compounds.

50 In mild alkaline medium, thiosulphate ion is oxidised by MnO_4^- to "A". The oxidation state of sulphur in "A" is ..... . **[2021, 26 Feb Shift-II]**

Ans. ***(6)***

$$\underset{\substack{\text{Thiosulphate ion}\\[\text{Reducing agent}]}}{S_2O_3^{2-}} + \underset{\substack{\text{Permanganate ion}\\[\text{Oxidising agent}]}}{MnO_4^-} \xrightarrow[\text{medium}]{\text{Mild Alkaline}} \underset{\substack{\text{Sulphate ion}\\(A)}}{SO_4^{2-}} + \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

Oxidation number of sulphur in SO_4^{2-} (A) is +6.

$$\left[\because\ x + 4(-2) = -2 \Rightarrow x = +6\right]$$

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51 On treating a compound with warm dil. H_2SO_4, gas *X* is evolved, which turns $K_2Cr_2O_7$ paper acidified with dil. H_2SO_4 to a green compound *Y*. *X* and *Y* respectively are

[2021, 26 Feb Shift-I]

(a) $X = SO_2, Y = Cr_2O_3$
(b) $X = SO_3, Y = Cr_2O_3$
(c) $X = SO_2, Y = Cr_2(SO_4)_3$
(d) $X = SO_3, Y = Cr_2(SO_4)_3$

Ans. ***(c)***

Gas, *X* turns acidified dichromate ($K_2Cr_2O_7$) green that means it is a reducing agent.

Cr (VI) from compound $K_2\overset{+6}{Cr_2}O_7$ on reduction changes its colour from orange to green which is the colour of Cr (III) compound *Y*.

$\overset{+4}{SO_2}$ can show both reducing and oxidising properties whereas $\overset{+6}{SO_3}$ cannot show reducing property because of highest group number 16, oxidation state (+6) of sulphur in SO_3.

So, *X* is SO_2.

As, *X* reacts with $K_2Cr_2O_7$ in dil. H_2SO_4 medium, the green coloured Cr (III) compound, *Y* must be Cr (III) sulphate or $Cr_2(SO_4)_3$.

So, *Y* is $Cr_2(SO_4)_3$.

The overall reactions can be shown as :

$$\underset{\text{Water soluble } SO_3^{2-} \text{ salt}}{(\text{Compound})} \xrightarrow[H_2SO_4]{\text{Dil.}} \xrightarrow[H_2SO_4]{\text{Dil.}} \underset{(X)}{SO_2(g)} \xrightarrow[\text{dil. } H_2SO_4]{K_2Cr_2O_7} \underset{(Y)\ (\text{Green})}{Cr_2(SO_4)_3}$$

(i) $SO_3^{2-} + H_2SO_4 \longrightarrow \underset{(X)}{SO_2}\uparrow + H_2O + SO_4^{2-}$

(ii) $\underset{(\text{Orange})}{K_2\overset{+6}{Cr_2}O_7} + \underset{(X)}{\overset{+4}{SO_2}} + H_2SO_4 \longrightarrow \underset{(Y)\ (\text{Green})}{\overset{+3}{Cr_2}(SO_4)_3} + K_2\overset{+6}{SO_4} + H_2O$

52 The incorrect statement is :

[2020, 3 Sep Shift-II]

(a) Manganate ion is green in colour and permanganate ion is purple in colour.
(b) Manganate and permanganate ions are paramagnetic.
(c) In manganate and permanganate ions, the π-bonding takes place by overlap of *p*-orbitals of oxygen and *d*-orbitals of manganese.
(d) Manganate and permanganate ions are tetrahedral.

Ans. ***(b)***

Statement (b) is incorrect whereas all other statements are correct.

Corrected statement is :

(b) Manganate ions contain 1 unpaired electron that it shows paramagnetic nature but permanganate ion, has no unpaired electron so, it shows diamagnetic nature.

Manganate	Permanganate
$\overset{+6}{MnO_4}^{2-}$	$\overset{+7}{MnO_4^{\ominus}}$
Hybridisation-p^3s	Hybridisation-p^3s
Colour - Green	Colour - Purple
Unpair $e^- = 1\ e^-$	Unpair $e^- =$ No unpair e^-
Magnetic nature = Paramagnetic	Magnetic nature = Diamagnetic

Other statements are discussed as follows :

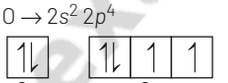
(a) Manganate ions contain 1 unpair electron that it show paramagnetic nature but in paramagnetic ion has no unpair electron, so it shows diamagnetic nature.

(c) $Mn \longrightarrow 3d^5 4s^2$

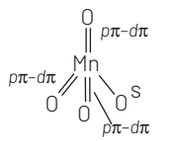
G.S.

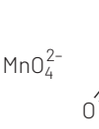
E.S.

$O \rightarrow 2s^2 2p^4$



Hybridisation is-d^3s
Shape-tetrahedral





It is same as MnO_4^- d^3s-hybridisation and tetrahedral shape.

In MnO_4^- and MnO_4^{2-}, the π-bonding take place by overlap of *p*-orbital of oxygen and *d*-orbital of Mn. This option is also correct.

(d) We have seen in option (c) manganate and permanganate ions are tetrahedral.
This option is also correct.

53 The incorrect statement(s) among (1)-(3) is (are)

1. W(VI) is more stable than Cr(VI).
2. in the presence of HCl, permanganate titrations provide satisfactory results.
3. some lanthanoid oxides can be used as phosphors.

[2020, 4 Sep Shift-II]

(a) 2 and 3 only (b) 2 only
(c) 1 only (d) 1 and 2 only

Ans. ***(b)***

Only statement 2 is incorrect, whereas 1 and 3 are correct.

$KMnO_4$ will not give satisfactory result when it is titrated by HCl, because same amount of $KMnO_4$ is consumed to oxidise HCl into Cl_2.

54 Consider the following reactions :

$NaCl + K_2Cr_2O_7 + H_2SO_4 \rightarrow (A) +$ side products (conc)

$(A) + NaOH \rightarrow (B) +$ side products

$(B) + H_2SO_4 + H_2O_2 \rightarrow (C) +$ side products (dilute)

The sum of the total number of atoms in one molecule each of (*A*), (*B*) and (*C*) is .....

[2020, 7 Jan Shift-II]

Ans. ***(18.00)***

Reactions : $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow \underset{(A)}{2CrO_2Cl_2} + 4NaHSO_4 + 2KHSO_4 + 3H_2O$

$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{(B)}{Na_2CrO_4} + 2NaCl + 2H_2O$

$Na_2CrO_4 + 2H_2SO_4 + 2H_2O_2 \longrightarrow \underset{(C)}{CrO_5} + 2NaHSO_4 + 3H_2O$

Number of atoms : (*A*) $CrO_2Cl_2 = 5$

(*B*) $Na_2CrO_4 = 7$

(*C*) $CrO_5 = 6$

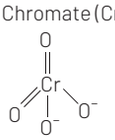
$\therefore \quad A + B + C = 18$

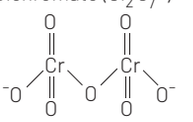
55 The sum of the total number of bonds between chromium and oxygen atoms in chromate and dichromate ions is .....

[2020, 9 Jan Shift-II]

Ans. ***(12.00)***

Chromate (CrO_4^{2-}) Dichromate ($Cr_2O_7^{2-}$)



4 Cr—O or 

8Cr—O

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Total number of bonds between chromium and oxygen atoms in chromate and dichromate ions = 4 + 8 = 12.

56 $\underline{A} \xrightarrow{4\,KOH,\ O_2} \underset{\text{(Green)}}{2\underline{B}} + 2H_2O$

$3\underline{B} \xrightarrow{4\,HCl} \underset{\text{(Purple)}}{2\underline{C}} + MnO_2 + 2H_2O$

$2\underline{C} \xrightarrow{H_2O,\ KI} 2\underline{A} + 2KOH + \underline{D}$

In the above sequence of reactions, $\underline{A}$ and $\underline{D}$, respectively, are **[2019, 11 Jan Shift-II]**

(a) KI and $KMnO_4$
(b) MnO_2 and KIO_3
(c) KI and K_2MnO_4
(d) KIO_3 and MnO_2

Ans. ***(b)***

When MnO_2(*A*) is fused with alkali in presence of air then potassium manganate (*B*) is forme(d) Potassium manganate (*B*) is of green colour which disproportionate in a neutral or acidic solution to produce potassium permanganate (*C*). Potassium permanganate (*C*) in presence of acidic medium oxidises iodide to iodate.

The reaction can be shown as :

(i) $\underset{(A)}{2\overset{+4}{Mn}O_2} \xrightarrow[\Delta]{4\,KOH,\ \overset{0}{O_2}} \underset{\substack{\text{Potassium manganate}\\\text{(Green)}}}{2K_2\overset{+6}{Mn}\overset{-2}{O}_4} + 2\overset{-2}{H_2O}$

(ii) $3\underset{(B)}{K_2\overset{+6}{Mn}O_4} \xrightarrow{4HCl} \underset{\substack{(C)\\\text{Potassium permanganate}\\\text{(Purple)}}}{2K\overset{+7}{Mn}O_4} + \overset{+4}{MnO_2} + 2H_2O + 4KCl$

(iii) $\underset{(C)}{2K\overset{+7}{Mn}O_4} \xrightarrow{K\overset{-1}{I},\ H_2O} \underset{(A)}{2\overset{+4}{Mn}O_2} + 2KOH + \underset{(D)}{K\overset{+5}{I}O_3}$

Thus, *A* and *D* are MnO_2 and KIO_3 respectively.

57 Thermal decomposition of a Mn compound (*X*) at 513 K results in compound (*Y*), MnO_2 and a gaseous product. MnO_2 reacts with NaCl and concentrated H_2SO_4 to give a pungent gas *Z*. *X*, *Y* and *Z*, respectively, are **[2019, 12 April Shift-II]**

(a) K_3MnO_4, K_2MnO_4 and Cl_2
(b) K_2MnO_4, $KMnO_4$ and SO_2
(c) $KMnO_4$, K_2MnO_4 and Cl_2
(d) K_2MnO_4, $KMnO_4$ and Cl_2

Ans. ***(c)***

Thermal decomposition of Mn compound (*X*), i.e. $KMnO_4$ at 513 K results in compound *Y* (i.e. K_2MnO_4), MnO_2 and a gaseous product. MnO_2 reacts with NaCl and concentrated H_2SO_4 to give a pungent gas *Z* (i.e. Cl_2). The reactions involved are as follows :

$\underset{(X)}{2KMnO_4} \xrightarrow[\Delta]{513\,K} \underset{(Y)}{K_2MnO_4} + MnO_2 + O_2(g)$

$MnO_2 + 4NaCl + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + \underset{(Z)\text{ pungent gas.}}{Cl_2(g)}$

58 The colour of $KMnO_4$ is due to **[JEE Main 2015]**

(a) $M \rightarrow L$ charge transfer transition
(b) $d - d$ transition
(c) $L \rightarrow M$ charge transfer transition
(d) $\sigma - \delta$ transition

Ans. ***(c)***

$KMnO_4 \longrightarrow K^+ + MnO_4^-$

$\therefore$ In MnO_4^-, Mn has +7 oxidation state having no electron in *d*-orbitals.

It is considered that higher the oxidation state of metal, greater is the tendency to occur $L \rightarrow M$ charge transfer, because ligand is able to donate the electrons into the vacant *d*- orbital of metal.

Since, charge transfer is Laporte as well as spin allowed, therefore, it shows colour.

Time Saving Technique *There is no need to check all the four options. Just find out the oxidation state of metal ion. If oxidation state is highest and ligand present there is of electron donating nature, gives LMCT, which shows more intense colour.*

59 Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect? **[AIEEE 2012]**

(a) Ferrous oxide is more basic in nature than the ferric oxide
(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds
(c) Ferrous compounds are less volatile than the corresponding ferric compounds
(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds

Ans. ***(d)***

(a) FeO > Fe_2O_3 (basic). Thus, it is correct statement.
(b) $FeCl_2$ > $FeCl_3$ (ionic), larger the charge greater the polarizing power. Thus, greater the covalent nature. Thus, the given statement is correct
(c) Fe^{2+} salts are more ionic thus less volatile than Fe^{3+} salts. Thus, given statement is correct.
(d) Greater the covalent nature, more easily they are hydrolyze(d) Thus, $FeCl_3$ is more hydrolyzed than $FeCl_2$.
Thus, statement (d) is incorrect.

60 Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the following statements is incorrect for this reaction? **[AIEEE 2004]**

(a) Cu_2I_2 is formed
(b) CuI_2 is formed
(c) $Na_2S_2O_3$ is oxidised
(d) Evolved I_2 is reduced

Ans. ***(b)***

$CuSO_4 + 2KI \longrightarrow \underset{\text{Unstable}}{CuI_2} + K_2SO_4$

$2CuI_2 \longrightarrow Cu_2I_2 + I_2$

Thus, CuI_2 is not formed.

TOPIC 3
Inner Transition Elements

61 The Eu^{2+} ion is a strong reducing agent in spite of its ground state electronic configuration (outermost) : [Atomic number of Eu = 63] **[2021, 31 Aug Shift-II]**

(a) $4f^7 6s^2$ (b) $4f^6$
(c) $4f^7$ (d) $4f^6 6s^2$

Ans. ***(c)***

The electronic configuration of Eu and Eu^{2+} ion is as follows :

$Eu(Z = 63) = [Xe]\,4f^7 6s^2$

$Eu^{2+}(Z = 63) = [Xe]\,4f^7$

62 Which one of the following lanthanides exhibits +2 oxidation state with diamagnetic nature ? (Given, *Z* for Nd = 60, Yb = 70, La = 57, Ce = 58) **[2021, 31 Aug Shift-I]**

(a) Nd (b) Yb
(c) La (d) Ce

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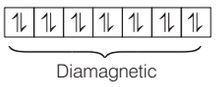
Ans. ***(b)***

Ytterbium shows +2 oxidation state and it is diamagnetic in nature.

$Yb = [Xe], 4f^{14}, 6s^2$

$Yb^{2+} = [Xe], 4f^{14}$

$Yb^{2+} = [Xe],$



Since, there is no unpaired electron, it is diamagnetic in nature.

63 The number of *f*-electrons in the ground state electronic configuration of Np ($Z = 93$) is ..... . (Nearest integer) **[2021, 27 Aug Shift-I**

Ans. ***(18)***

The electronic configuration of Np = 93 is

$1s^2\ 2s^2 2p^6 3s^2 3p^6 3d^{10}\ 4s^2 4p^6 4d^{10}\ 5s^2 5p^6\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^6\ 5f^4\ 6d^1 7s^2$

In ground state, total number of *f* electrons = 14 + 4 = 18

64 The number of 4*f* electrons in the ground state electronic configuration of Gd^{2+} is

[Atomic number of Gd is 64.]

[2021, 26 Aug Shift-I]

Ans. ***(7)***

The electronic configuration of Gd is as follows

$Gd = [Xe]\, 4f^7, 5d^1, 6s^2$

So, electronic configuration of Gd^{2+} will be

$Gd^{2+} = [Xe], 4f^7, 5d^1, 6s^0$

∴ The number of 4*f* electrons in ground state configuration of Gd^{2+} is 7.

65 Number of electrons present in 4*f* orbital of Ho^{3+} ion is ..... . (Given, atomic number of Ho = 67)

[2021, 25 July Shift-II]

Ans. ***(10)***

Holmium is *f*-block element (actinide) having atomic number 67.

Ho(Holmium) = $[Xe]\, 4f^{11} 6s^2$

Electronic configuration of $Ho^{3+} = [Xe]\, 4f^{10} 6s^0$

So, number of electrons present in 4*f* is 10.

66 Given below are two statements.

Statement I The $E°$ value of Ce^{4+}/Ce^{3+} is +1.74 V.

Statement II Ce is more stable in Ce^{4+} state than Ce^{3+} state.

In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 16 March Shift-I]

(a) Both statement I and statement II are correct.
(b) Statement I is incorrect but statement II is correct.
(c) Both statement I and statement II are incorrect.
(d) Statement I is correct but statement II is incorrect.

Ans. ***(d)***

$E°_{Ce^{4+}/Ce^{+3}} = 1.74$ (data given)

Ce^{4+} can be reduced to Ce^{3+} and can oxidise water.

$$Ce^{4+} + e^- \longrightarrow Ce^{3+}$$

Ce^{4+} is having noble gas configuration $[Xe]4f^0$ but it is strong oxidant and gets converted to Ce^{3+}.

Statement I is correct but statement II is incorrect.

67 Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Size of Bk^{3+} ion is less than Np^{3+} ion.

Reason (R) The above is a consequence of the lanthanoid contraction. In the light of the above statements, choose the correct answer from the options given below **[2021, 16 March Shift-I]**

(a) A is false but R is true.
(b) Both A and R are true but *R* is not the correct explanation of (a)
(c) Both A and R are true and R is the correct explanation of (a)
(d) A is true but R is false.

Ans. ***(d)***

$_{97}Bk$ (Berkelium) and $_{93}Np$ (Neptunium) are present in actinide series. Due to actinoid contraction, there is gradual decrease in size of M^{3+} ions across the period due to poor shielding of 5*f*-electrons.

So, Bk^{3+} is smaller than that of Np^{3+} due to actinoid contraction.

So, A is true and R is false.

68 Which one of the following lanthanoids does not form MO_2? [*M* is lanthanoid metal]

[2021, 26 Feb Shift-I]

(a) Pr (b) Dy (c) Nd (d) Yb

Ans. ***(d)***

In oxides, MO_2 (*M* is lanthanoid metal) only four lanthanoids exhibit + 4 oxidation state. These lanthanoids are praseodymium (Pr, $Z = 59$), neodymium (Nd, $Z = 60$) terbium (Tb, $Z = 65$) dysprosium (Dy, $Z = 66$).

So, Yb(ytterbium) option (d) does not form MO_2 type of oxide.

Note The common and predominant oxidation state of lanthanoids is +3. Consequently M^{4+} compounds are strong oxidising agents which changes to the common +3 state. Similarly, lanthanoid compounds of +2 state have a tendency to show reducing property as they get changed to +3 state easily.

69 Given below are two statements:

Statement I CeO_2 can be used for oxidation of aldehydes and ketones.

Statement II Aqueous solution of $EuSO_4$ is a strong reducing agent.

In the light of the above statements, choose the correct answer from the options given below. **[2021, 25 Feb Shift-I]**

(a) Both statement I and statement II are true.
(b) Both statement I and statement II are false.
(c) Statement I is true but statement II is false.
(d) Statement I is false but statement II is true.

Ans. ***(a)***

Both statement I and statement II are true. The +3 oxidation state of lanthanide is most stable and therefore lanthanide in + 4 oxidation state has strong tendency to gain electrons and converted into + 3 and therefore act as strong oxidising agent, e.g. Ce^{4+}.

∴ CeO_2 is used to oxidised alcohol, aldehyde and ketones.

Lanthanides in + 2 oxidation state has strong tendency to loss electron and converted into + 3 oxidation state e.g. Eu^{+2}.

∴ $EuSO_4$ acts as strong reducing agent.

70 The elements with atomic numbers 101 and 104 belong to, respectively,

[2020, 4 Sep Shift-I]

(a) actinoids and group 4
(b) actinoids and group 6
(c) group 6 and actinoids
(d) group 11 and group 4

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Ans. *(a)*

Actinoid series have atomic number from 90 to 103 (*f*-block element).

So, element with atomic number (*Z*) 101 belongs to actinoid series and elements with atomic number (*Z*) 104 belongs to 4th group.

71 The lanthanoid that does not show +4 oxidation state is **[2020, 6 Sep Shift-I]**

(a) Dy (b) Ce (c) Eu (d) Tb

Ans. *(c)*

Europium (Eu = atomic number 63)

Electronic configuration of Eu = $[Xe]4f^7, 6s^2$

It can show +2 and +3 oxidation state

in +2 oxidation: $Eu^{2+} = [Xe]4f^7, 6s^0$

in +3 oxidation : $Eu^{3+} = [Xe]4f^6, 6s^0$

Being a typical member of the lanthanide, Eu usually assumes the oxidation state +3 and +2 but it doesn't show +4 oxidation state due to very high ionisation energy (4140 kJ/mol).

Hence, the correct option is (c).

72 Mischmetal is an alloy consisting mainly of **[2020, 6 Sep Shift-II]**

(a) lanthanoid metals
(b) actinoid and transition metals
(c) lanthanoid and actinoid metals
(d) actinoid metals

Ans. *(a)*

Lanthanoids are used in the production of alloy steels to improve the strength and work ability of steel. A well known alloy is mischmetal which has the following composition.

Mischmetal – lanthanoid metals = 95%

(About 40% La, 50% Ce and the rest other lanthanoids) with traces of iron = 5%

S, C, Ca and Al.

73 The highest possible oxidation states of uranium and plutonium, respectively, are **[2019, 10 April Shift-II]**

(a) 7 and 6 (b) 6 and 7
(c) 6 and 4 (d) 4 and 6

Ans. *(b)*

Actinoids show a variety of oxidation states due to comparable energies of 5*f*, 6*d* and 7*s* energy levels.

In the actinoids family (5*f*-block), uranium (U) neptunium (Np), plutonium (Pu) and americium (Am) have highest possible oxidation states of +6, + 7, + 7 and +6 respectively.

74 The effect of lanthanoid contraction in the lanthanoid series of elements by and large means **[2019, 10 Jan Shift-I]**

(a) increase in atomic radii and decrease in ionic radii
(b) decrease in both atomic and ionic radii
(c) increase in both atomic and ionic radii
(d) decrease in atomic radii and increase in ionic radii

Ans. *(b)*

Lanthanoid contraction in the lanthanoid series takes place due to the presence of electron(s) in the 4*f*-orbitals. *f*-orbitals have poor shielding effect. As a result, the effective nucleur charge will be more experienced by the 5*d* and 6*s*- electrons and it will cause contraction or decrease in both atomic and ionic radii.

75 The correct order of atomic radii is **[2019, 12 Jan Shift-II]**

(a) Ho > N > Eu > Ce
(b) N > Ce > Eu > Ho
(c) Eu > Ce > Ho > N
(d) Ce > Eu > Ho > N

Ans. *(c)*

The correct order of atomic radii is

Europium (Eu) (199 pm) > Cerium (Ce) (183 pm) > Holmium (Ho) (176 pm) > Nitrogen (N) (65 pm)

Note

(i) N being the member of *p*-block and second period, have the smallest radii.
(ii) Rest of all the 3 members are lanthanides with Eu having stable half-filled configuration thus with bigger size than rest two.
(iii) Among Ce and Ho, Ce has larger size which can be explained on the basis of "Lanthanoid contraction".

76 The atomic radius of Ag is closest to **[2020, 7 Jan Shift-I]**

(a) Hg (b) Au (c) Ni (d) Cu

Ans. *(b)*

The atomic radii of Ag is almost equal to Au due to lanthanide contraction.

77 In context of the lanthanoids, which of the following statements is not correct?

(a) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
(b) All the member exhibit +3 oxidation state.
(c) Because of similar properties the separation of lanthanoids is not easy.
(d) Availability of 4*f* electrons results in the formation of compounds in +4 state for all the members of the series. **[AIEEE 2011]**

Ans. *(d)*

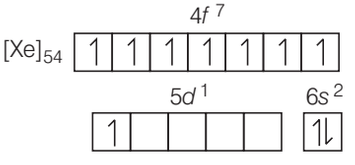
(a) There is a gradual decrease in the radii of the lanthanoids with increasing atomic number — a case of lanthanide contraction, thus true.
(b) Ionisation potential for the formation of Lu^{3+} is comparatively low, hence +3 state is favourable, thus true.
(c) Due to lanthanoide contraction–Zr and Hf; Nb and Ta, Mo and W have the same size and thus similar properties and thus separation is not easy, thus true.
(d) Formation of +4 state requires very high energy, thus incorrect.

78 The outer electron configuration of Gd (At. no. 64) is **[AIEEE 2011]**

(a) $4f^3, 5d^5, 6s^2$ (b) $4f^8, d^0, 6s^2$
(c) $4f^4, 5d^4, 6s^2$ (d) $4f^7, 5d^1, 6s^2$

Ans. *(d)*

Gd (64)



All the electrons in 4*f*-orbital are unpaired, hence stable. Thus, Gd (64) has EC as $[Xe]_{54}\ 4f^7, 5d^1, 6s^2$

Instead of $[Xe]_{54}\ 4f^8, 6s^2$.

79 Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect? **[AIEEE 2009]**

(a) Because of the large size of the Ln (III) ions the bonding in its its compounds is predominantly ionic in character
(b) The ionic sizes of Ln (III) decrease in general with increasing atomic number

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(c) Ln (III) compounds are generally colourless
(d) Ln (III) hydroxide are mainly basic in character

Ans. ***(c)***

The most common oxidation state of lanthanoid is +3. Lanthanoids in +3 oxidation state usually have unpaired electron in *f*-subshell and impart characteristic colour in solid as well as in solution state due to *f*-*f* transition. (Except lanthanum and lutetium)

80 Larger number of oxidation states are exhibited by the actinoides than those by the lanthanoides, the main reason being **[AIEEE 2008]**
(a) 4*f* orbitals more diffused than the 5*f* orbitals
(b) lesser energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals
(c) more energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals
(d) more reactive nature of the actinoides than the lanthanoides

Ans. ***(b)***

Lanthanoides : $[Xe]4f^{1-14}5d^{0-1}6s^2$
Actinoides : $[Rn]5f^{1-14}6d^{0-1}7s^2$
Lanthanoides and actinoides use core *d* and *f* orbitals also to show higher oxidation state. As actinoides have comparatively low energy difference between *f* and *d* orbitals, thus, they show more number of oxidation states.

81 Identify the incorrect statement among the following. **[AIEEE 2007]**
(a) *d*-block elements show irregular and erratic chemical properties among themselves
(b) La and Lu have partially filled *d* orbitals and no other partially filled orbitals
(c) The chemistry of various lanthanoids is very similar
(d) 4*f* and 5*f* orbitals are equally shielded

Ans. ***(d)***

4*f* orbital is nearer to nucleus as compared to 5*f* orbital. Therefore, shielding of 4*f* is more than 5*f* orbital.

82 The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because **[AIEEE 2007]**
(a) the 5*f* orbitals are more buried than the 4*f* orbitals
(b) there is a similarity between 4*f* and 5*f* orbitals in their angular part of the wave function
(c) the actinoids are more reactive than the lanthanoids
(d) the 5*f* orbitals extend farther from the nucleus than the 4*f* orbitals

Ans. ***(d)***

The actinoids (5*f*-element) exhibit more number of oxidation states in general than the lanthanoids because 5*f* orbitals extend farther from the nucleus than the 4*f*-orbitals.
Thus, the attraction on the 5*f* electrons in actinoid series decreases. Hence, they can easily participate in bonding and therefore, exhibits more number of oxidation states.

83 Lanthanoid contraction is caused due to
(a) the appreciable shielding on outer electrons by 4*f* electrons from the nuclear charge
(b) the appreciable shielding on outer electrons by 5*d* electrons from the nuclear charge
(c) the same effective nuclear charge from Ce to Lu
(d) the imperfect shielding on outer electrons by 4*f* electrons from the nuclear charge **[AIEEE 2006]**

Ans. ***(d)***

Imperfect shielding on outer electrons by 4*f* electrons from the nuclear charge is due to the diffused large shape of 4*f*-orbitals.
This imperfect shielding is unable to counterbalance the effect of the increased nuclear charge. Hence, the net result shows contraction in size.

84 Which of the following factors may be regarded as the main cause of lanthanide contraction? **[AIEEE 2005]**
(a) Greater shielding of 5*d* electron by 4*f* electrons
(b) Poorer shielding of 5*d* electron by 4*f* electrons
(c) Effective shielding of one of 4*f* electron by another in the subshell
(d) Poor shielding of one of 4*f* electron by another in the subshell

Ans. ***(d)***

Lanthanide contraction is due to poor shielding of one of 4*f* electron by another in the sub-shell.

85 Cerium ($Z = 58$) is an important member of the lanthanides. Which of the following statements about cerium is incorrect?
(a) The common oxidation states of cerium are +3 and +4 **[AIEEE 2004]**
(b) The +3 oxidation state of cerium is more stable than the +4 oxidation state
(c) The +4 oxidation state of cerium is not known in solutions
(d) Cerium (IV) acts as an oxidising agent

Ans. ***(c)***

+3 and +4 states are shown by Ce in aqueous solution. Thus, statement (c) is incorrect.

86 The radius of La^{3+} (atomic number : La = 57) is 1.06 Å. Which one of the following given values will be closest to the radius of Lu^{3+} (atomic number : Lu = 71)? **[AIEEE 2003]**
(a) 1.60Å (b) 1.40 Å
(c) 1.06 Å (d) 0.85 Å

Ans. ***(d)***

Due to lanthanide contraction, there occurs net decrease in size. Only, 0.85 Å is smaller one.

87 Most common oxidation states of Ce (Cerium) are **[AIEEE 2002]**
(a) + 3, + 4
(b) + 2, + 3
(c) + 2, + 1
(d) + 3, + 5

Ans. ***(a)***

Cerium, $Ce_{58} = [Xe]4f^1 5d^1 6s^2$. Its most stable oxidation state is +3 but +4 is also existing.

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19

Coordination Compounds

TOPIC 1
Nomenclature, Isomerism and Werner's Theory

01 Spin only magnetic moment in BM of $[Fe(CO)_4(C_2O_4)]^+$ is

[2021, 31 Aug Shift-II]

(a) 5.92 (b) 0
(c) 1 (d) 1.73

Ans. ***(d)***

In $[Fe(CO)_4(C_2O_4)]^+$, oxidation number of Fe = +3

$\{x + 4 \times 0 + (-2) = 1$

$\therefore \quad x = 3$

$Fe^{3+} = [Ar]3d^5 4s^0$

CO is a strong field ligand, so pairing is favoured

$Fe^{3+} = t_{2g}^{2,2,1}, e_g^{0,0}$

Number of unpaired electron $(n) = 1$

$\mu = \sqrt{n(n+2)}$ BM

$= \sqrt{1(1+2)}$

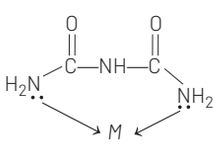
$= \sqrt{3} = 1.73$ BM

02 The denticity of an organic ligand, biuret is **[2021, 31 Aug Shift-I]**

(a) 2 (b) 4
(c) 3 (d) 6

Ans. ***(a)***

Biuret is bidentate ligand and denticity of this organic ligand is 2.



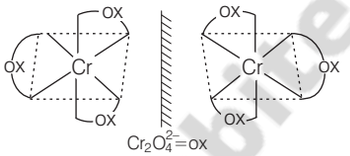
Hence, correct option is (a).

03 The number of optical isomers possible for $[Cr(C_2O_4)_3]^{3-}$ is ...

[2021, 27 Aug Shift-II]

Ans. ***(2)***

The structure of $[Cr(C_2O_4)_3]^{3-}$ is



Mirror image optical isomers

Oxalate is bidentate symmetrical ligand. The complex does not possess any element of symmetry and are optically active. The two optical isomers are shown above.

$\therefore$ Answer is two (2).

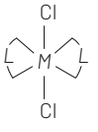
04 1 mol of an octahedral metal complex with formula $MCl_3 \cdot 2L$ on reaction with excess of $AgNO_3$ gives 1 mol of AgCl. The denticity of ligand *L* is ..... . (Integer answer)

[2021, 27 Aug Shift-I]

Ans. ***(2)***

Since, the compound is octahedral, the central metal *M* will form 6 bonds. On reaction with excess of $AgNO_3$, only 1 mol of AgCl is precipitated that means only 1 Cl^- is present as counter ion and 2Cl^- ions are present in coordinate sphere.

So '*L*' should by bidentate to form an octahedral complex alongwith 2Cl^- ions.



$[MCl_2L_2]Cl$

05 3 moles of metal complex with formula $Co(en)_2Cl_3$ gives 3 moles of silver chloride on treatment with excess of silver nitrate. The secondary valency of Co in the complex is ..... .

(Round off to the nearest integer)

[2021, 27 July Shift-II]

Ans. ***(6)***

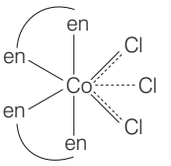
1 mole of $[Co(en)_2Cl_3]$ produces 1 mole of AgCl.

3 moles of $[Co(en)_2Cl_3]$ produces 3 moles of AgCl.

$\therefore$ Given compound is $[Co(en)_2Cl_2]Cl$.

$[Co(en)_2Cl_2]Cl(aq) + AgNO_3(aq) \longrightarrow$ (excess)

$[Co(en)_2Cl_2]NO_3(aq) + AgCl(s) \downarrow$ (white)



Dotted line represents primary valency = 3.

Solid line represents secondary valency (coordinated ions) of Co = 6.

06 Given below are two statements.

Statement I $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are d^2sp^3 hybridised.

Statement II $[MnCl_6]^{3-}$ and $[FeF_6]^{3-}$ are paramagnetic and have 4 and 5 unpaired electrons, respectively.

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In the light of the above statements, choose the correct answer from the options given below **[2021, 27 July Shift-II]**

(a) Statement I is true but statement II is false
(b) Both statement I and statement II are false
(c) Statement I is false but statement II is true
(d) Both statement I and statement II are true

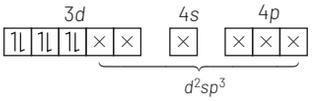
Ans. ***(d)***

Hybridisation of all the given complexes are given in following table.

$[Mn(CN)_6]^{3-} \Rightarrow Mn^{3+}$

CN^- is a strong field ligand.

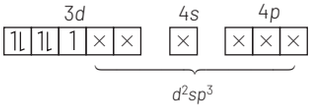
∴Pairing of electron takes place.



$[Fe(CN)_6]^{3-} \Rightarrow Fe^{3+}$

CN^- is a strong ligand.

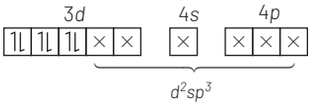
∴Pairing of electron takes place.



$[Co(C_2O_4)_3]^{3-} \Rightarrow Co^{3+}$

$C_2O_4^{2-}$ acts as strong field ligand with Co^{3+}.

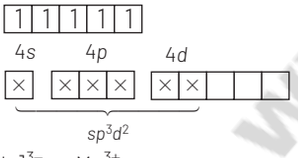
∴Pairing of electrons takes place.



$[FeF_6]^{3-} \Rightarrow Fe^{3+}$

F is a weak field ligand.

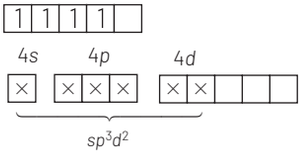
∴Pairing of electron does not occurs.



$[MnCl_6]^{3-} \Rightarrow Mn^{3+}$

Cl^- is a weak field ligand.

∴Pairing of electron does not occurs.



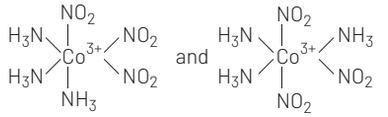
$[FeF_6]^{3-}$ have 5 unpaired electrons and $[MnCl_6]^{3-}$ have 4 unpaired electrons.

So, both statement I and statement II are true.

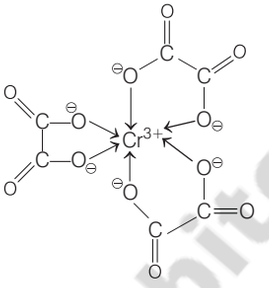
07 The number of geometrical isomers possible in triamminetrinitrocobalt (III) is *X* and in trioxalatochromate (III) is *Y*. Then, the value of $X + Y$ is ..... . **[2021, 27 July Shift-I]**

Ans. ***(2)***

Formula of triamminetrinitrocobalt (III) is $[Co(NO_2)_3(NH_3)_3]$. Its geometrical isomers are as follows



The formula of trioxalatochromate (III) ion is $[Cr(C_2O_4)_3]^{3-}$. It has no geometrical isomers.



Zero geometrical isomer

Thus, the value of $X + Y = 2 + 0 = 2$

08 An organic compound is subjected to chlorination to get compound *A* using 5.0 g of chlorine. When 0.5 g of compound *A* is reacted with $AgNO_3$ [Carius method], the percentage of chlorine in compound *A* is ..... when it forms 0.3849 g of AgCl. (Round off to the nearest integer)

(Atomic masses of Ag and Cl are 107.87 and 35.5 respectively) **[2021, 27 July Shift-I]**

Ans. ***(19)***

Mass of organic compound = 0.5 g

Mass of AgCl formed = 0.3849 g

$$\% \text{ of Cl} = \frac{\left(\begin{array}{c}\text{Atomic mass of Cl}\\ \times \text{ Mass of AgCl formed}\end{array}\right)}{\left(\begin{array}{c}\text{Molecular mass of AgCl}\\ \times \text{ Mass of organic compound}\end{array}\right)} \times 100$$

$$= \frac{35.5 \times 0.3849}{143.37 \times 0.5} \times 100$$

$$= 19.06 \simeq 19$$

09 The number of geometrical isomers found in the metal complexes $[PtCl_2(NH_3)_2]$, $[Ni(CO)_4]$, $[Ru(H_2O)_3Cl_3]$ and $[CoCl_2(NH_3)_4]^+$ respectively, are **[2021, 27 July Shift-I]**

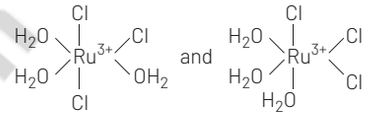
(a) 1, 1, 1, 1 (b) 2, 1, 2, 2
(c) 2, 0, 2, 2 (d) 2, 1, 2, 1

Ans. ***(c)***

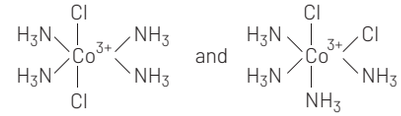
Number of geometrical isomers of $[PtCl_2(NH_3)_2]$ two geometrical isomers.

In $[Ni(CO)_4]$ complex all ligands are same. Therefore, it does not show geometrical isomers.

$[Ru(H_2O)_3Cl_3]$ two geometrical isomers.



$[CoCl_2(NH_3)_4]^+$ two geometrical isomers.



10 The type of hybridisation and magnetic property of the complex $[MnCl_6]^{3-}$, respectively, are **[2021, 27 July Shift-I]**

(a) sp^3d^2 and diamagnetic
(b) d^2sp^3 and diamagnetic
(c) d^2sp^3 and paramagnetic
(d) sp^3d^2 and paramagnetic

Ans. ***(d)***

The type of hybridisation and magnetic property of $[MnCl_6]^{3-}$ are sp^3d^2 and paramagnetic respectively.

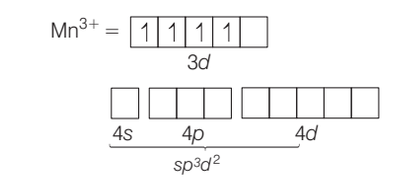
In $[MnCl_6]^{3-}$, oxidation state of Mn is

$$x + 6(-1) = -3$$

$$x = -3 + 6 \Rightarrow x = +3$$

Electronic configuration of Mn is $[Ar]3d^54s^2$.

Electronic configuration $Mn^{3+} = [Ar]3d^4$



As Cl is a weak field ligand, so no pairing of electrons occurs.

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Thus, hybridisation is sp^3d^2.

Magnetic behaviour is paramagnetic (having 4 unpaired electrons).

11 Indicate the complex/complex ion which did not show any geometrical isomerism. **[2021, 26 Aug Shift-II]**

(a) $[CoCl_2(en)_2]$
(b) $[Co(CN)_5(NC)]^{3-}$
(c) $[Co(NH_3)_3(NO_2)_3]$
(d) $[Co(NH_3)_4Cl_2]^+$

Ans. ***(b)***

(a) $[CoCl_2(en)_2]$ shows *cis-trans* isomerism.

(b) $[Co(CN)_5(NC)]^{3-}$ is of MA_5B type complex, which will not show any isomerism.

(c) $[Co(NH_3)_3(NO_2)_3]$ shows *facial* and *meridonial* isomerism.

(d) $[Co(NH_3)_4Cl_2]^+$ shows geometrical (*cis-trans*) isomerism. In *cis* isomer, two Cl ligands are adjacent to each other. In *trans* isomer two Cl ligands are opposite to each other.

$\therefore$ Option (b) is correct.

12 Which one of the following metal complexes is most stable? **[2021, 25 July Shift-II]**

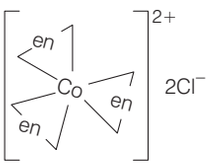
(a) $[Co(en)(NH_3)_4]Cl_2$
(b) $[Co(en)_3]Cl_2$
(c) $[Co(en)_2(NH_3)_2]Cl_2$
(d) $[Co(NH_3)_6]Cl_2$

Ans. ***(b)***

Stability of a complex depends on the chelating effect. Complex $[Co(en)_3]Cl_2$ is most stable complex among the given complex compounds because more number of chelate rings are present in this complex as compare to others.

(a) $[Co(en)(NH_3)_4]Cl_2$	1 chelate ring
(b) $[Co(en)_3]Cl_2$	3 chelate ring
(c) $[Co(en)_2(NH_3)_2]Cl_2$	2 chelate ring
(d) $[Co(NH_3)_6]Cl_2$	0 chelate ring

The structure of $[Co(en)_3]Cl_2$ is



13 Three moles of AgCl get precipitated when one mole of an octahedral co-ordination compound with empirical formula $CrCl_3 \cdot 3NH_3 \cdot 3H_2O$ reacts with excess of silver nitrate. The number of chloride ions satisfying the secondary valency of the metal ion is ..... . **[2021, 25 July Shift-I]**

Ans. ***(0)***

No. of mole of AgCl precipitated is equal to the mole of Cl^- present in ionisation sphere.

Now, reaction is

$$\underset{1\text{ mol}}{[Cr(H_2O)_3(NH_3)_3]Cl_3} \longrightarrow$$

$$\underset{1\text{ mol}}{[Cr(H_2O)_3(NH_3)_3]^{3+}} + \underset{3\text{ mol}}{3Cl^-} \xrightarrow[\text{excess}]{AgNO_3} \underset{3\text{ mol}}{AgCl}$$

Since, there is no Cl^- present in the coordination sphere. Therefore, zero chloride ions satisfy the secondary valency of the metal ion.

14 Which one of the following species responds to an external magnetic field **[2021, 25 July Shift-I]**

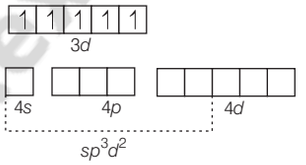
(a) $[Fe(H_2O)_6]^{3+}$ (b) $[Ni(CN)_4]^{2-}$
(b) $[Co(CN)_6]^{3-}$ (d) $[Ni(CO)_4]$

Ans. ***(a)***

Only paramagnetic substance or complex response to external magnetic field.

(a) $\mathbf{[Fe(H_2O)_6]^{3+}}$; Electronic configuration of $Fe^{3+} = [Ar]3d^5\,4s^0$

All electrons are unpaired (No pairing as H_2O is (a weak field ligand)



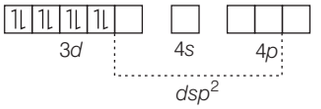
Hybridisation = sp^3d^2 (octahedral),

Unpaired electrons = 5

Magnetic nature = Paramagnetic (so this complex response to external magnetic field)

(b) $\mathbf{[Ni(CN)_4]^{2-}}$ Electronic configuration of $Ni^{2+} = [Ar]3d^8\,4s^0$

CN^- is a strong field ligand therefore, pairing of electrons occur.



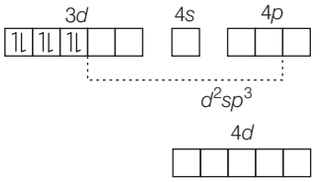
Hybridisation = dsp^2 (square planar)

Unpaired electron = 0 (all paired)

Magnetic nature = Diamagnetic

(c) $\mathbf{[Co(CN)_6]^{3-}}$; Electronic configuration of $Co^{3+} = [Ar]3d^6\,4s^0$

CN^- is a strong field ligand so, pairing of electrons occur.



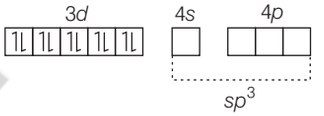
Hybridisation = d^2sp^3 (Octahedral)

Unpaired electrons = 0 (all paired)

Magnetic nature = Diamagnetic

(d) $\mathbf{[Ni(CO)_4]}$ Electronic configuration of Ni = $[Ar]3d^8\,4s^2$

CO is a strong field ligand so, pairing of electrons occur.



Hybridisation = sp^3 (tetrahedral)

Unpaired electron = 0

Magnetic nature = Diamagnetic

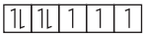
15 The total number of unpaired electrons present in $[Co(NH_3)_6]Cl_2$ and $[Co(NH_3)_6]Cl_3$ is ..... . **[2021, 22 July Shift-II]**

Ans. ***(1)***

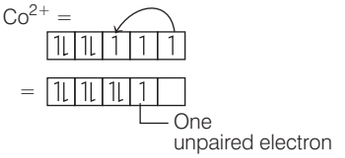
(i) $[Co(NH_3)_6]Cl_2 \Rightarrow$ Oxidation state of cobalt Co^{2+} is +2.

Electronic configuration $_{27}Co = [Ar]4s^2\,3d^7$

$Co^{2+} = [Ar]4s^0\,3d^7$ i.e.



NH_3 acts as SFL (strong field ligand) due to small size of cobalt with +2 charge, so pairing will took place.

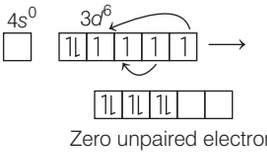


Co^{2+} have one unpaired electron.

(ii) $[Co(NH_3)_6]Cl_3 \Rightarrow$ Oxidation state of cobalt (CO^{2+}) is +3.

So, NH_3 acts as strong field ligand.

Hence, $Co^{3+} \longrightarrow 4s^0\,3d^6$



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Co^{3+} have zero unpaired electron.

$[Co(NH_3)_6]Cl_2 \Rightarrow Co^{2+} \rightarrow 3d^7$

(S.F.L) $n = 1$

$[Co(NH_3)_6]Cl_3 \Rightarrow Co^{3+} \rightarrow 3d^6$

(S.F.L) $n = 0$

So, total $(1+0) = 1$ unpaired electron.

16 The correct order of intensity of colors of the compound is

[2021, 20 July Shift-I]

(a) $[Ni(CN)_4]^{2-} > [NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+}$

(b) $[Ni(H_2O)_6]^{2+} > [NiCl_4]^{2-} > [Ni(CN)_4]^{2-}$

(c) $[NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+} > [Ni(CN)_4]^{2-}$

(d) $[NiCl_4]^{2-} > [Ni(CN)_4]^{2-} > [Ni(H_2O)_6]^{2+}$

Ans. ***(c)***

Correct order of intensity of colours of the compounds is

$[NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+} > [Ni(CN)_4]^{2-}$

Ni is in +2 oxidation state in all complexes. The intensity of colour depends on the strength of the ligand attached with the central metal atom because more strong ligand more splitting energy, less is intensity of colour. Strength of ligand is in the order $CN^- > H_2O > Cl^-$.

Splitting energy order $[NiCl_4]^{2-} < [Ni(H_2O)_6]^{2+} < [Ni(CN)_4]^{2-}$

$\therefore$ Intensity of colour of compound

$[NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+} > [Ni(CN)_4]^{2-}$

17 According to the valence bond theory the hybridisation of central metal atom is dsp^2 for which one of the following compounds?

[2021, 20 July Shift-I]

(a) $NiCl_2 \cdot 6H_2O$ (b) $K_2[Ni(CN)_4]$

(c) $[Ni(CO)_4]$ (d) $Na_2[NiCl_4]$

Ans. ***(b)***

According to VBT i.e. valence bond theory,

Electronic configuration of Ni = $[Ar]3d^8 4s^2$.

(a) **$NiCl_2 \cdot 6H_2O$**

$NiCl_2 \cdot 6H_2O \longrightarrow NiCl_2 + 6H_2O$

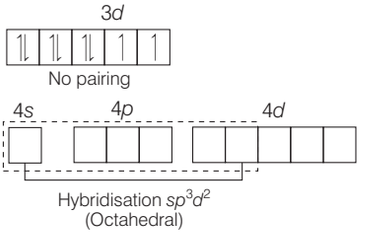
Oxidation number of Ni(x) = $x + 2(-1) = 0$; where x, -1 and 2 are the oxidation number of Ni, oxidation number of Cl and number of Cl atoms respectively.

$NiCl_2 \Rightarrow x + (-2) = 0 \Rightarrow x = 2$

Electronic configuration of $Ni^{2+} = [Ar]3d^8 4s^0$

Cl^- is a weak field ligand. So, no pairing of electrons occurs.

For C.N. = 6



(b) **$K_2[Ni(CN)_4]$**

$K_2[Ni(CN)_4] \longrightarrow 2K^+ + [Ni(CN)_4]^{2-}$

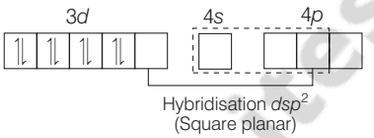
$x + 4(-1) - (-2) = 0$; where x, 4, -1 and -2 are the oxidation number of Ni, number of CN ligands, charge on one CN and charge on complex.

$[Ni(CN)_4]^{2-} \Rightarrow x - 4 + 2 = 0 \Rightarrow x = +2$

Electronic configuration of $Ni^{2+} \Rightarrow [Ar]3d^8 4s^0$

CN^- is a strong field ligand. So, pairing of electrons occur.

For C.N. = 4



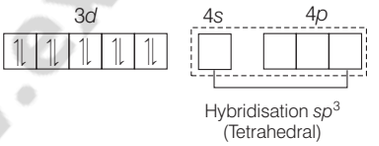
(c) **$Ni(CO)_4$**

CO is neutral and strong field ligand. So, pairing of electrons occur.

Oxidation number of Ni is zero

Electronic configuration of Ni = $[Ar]3d^{10}4s^0$

For C.N. = 4



(d) **$Na_2[NiCl_4]$**

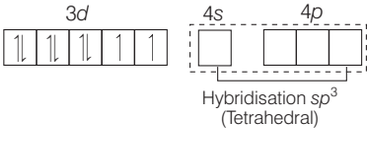
$Na_2[NiCl_4] \longrightarrow 2Na + [NiCl_4]^{2-}$

$x + 4(-1) - (-2) = 0$; where x, 4, -1 and -2 are the oxidation number of Ni, number of CN ligands, charge on one CN and charge on complex.

$[NiCl_4]^{2-} \Rightarrow x - 4 + 2 = 0 \Rightarrow x = +2$

Electronic configuration of $Ni^{2+} = [Ar]3d^8 4s^0$

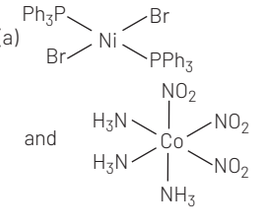
For C.N. = 4



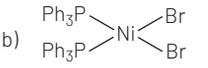
Hence, only $K_2[Ni(CN)_4]$ has dsp^2 hybridisation.

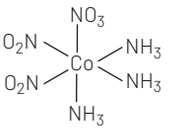
18 The correct structures of *trans*-$[NiBr_2(PPh_3)_2]$ and meridonial-$[Co(NH_3)_3(NO_2)_3]$, respectively are

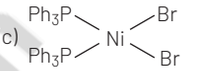
[2021, 18 March Shift-I]

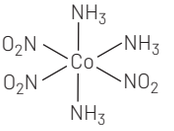
(a) 

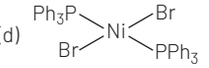
and

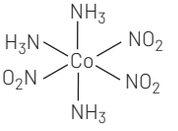
(b) 

and 

(c) 

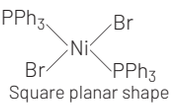
and 

(d) 

and 

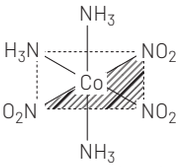
Ans. ***(d)***

Trans $[Ni\,Br_2(PPh_3)_2]$



Square planar shape

and meridional $[Co(NH_3)_3(NO_2)_3]$



Meridional (mer)
[*trans*]

19 Match List-I and List-II.

List-I	List-II
A. $[Co(NH_3)_6][Cr(CN)_6]$	1. Linkage isomerism
B. $[Co(NH_3)_3(NO_2)_3]$	2. Solvate isomerism
C. $[Cr(H_2O)_6]Cl_3$	3. Co-ordination isomerism
D. *cis*-$[CrCl_2(ox)_2]^{3-}$	4. Optical isomerism

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Choose the correct answer from the options given below.

[2021, 17 March Shift-II]

	A	B	C	D		A	B	C	D
(a)	3	1	2	4	(b)	4	2	3	1
(c)	2	1	3	4	(d)	1	2	3	4

Ans. ***(a)***

(A)-3, (B)-1, (C)-2, (D)-4

A. Coordination isomerisms occurs in coordination salts in which there is an interchange of ligands between the metal in the cationic coordination spheres and the metal in the anionic coordination sphere.
$[Co(NH_3)_6][Cr(CN)_6] \Leftrightarrow [Co(CN)_6][Cr(NH_3)_6]$ (Coordinate isomerism)

B. Linkage isomerism occurs in coordination compounds that have the same composition but differ in the connectivity of the ligand to the metal.
$[Co(NH_3)_3(NO_2)_3]$ shows linkage isomerism. NO_2 can connect through N and O donor sites.

C. Solvate isomerism is also known as 'hydrate isomerism' where water behaves as a ligand and water of crystallisation.
e.g., The complex $[Cr(H_2O)_6]Cl_3$ (violet) contains water as a ligand and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2H_2O$ (grey-green) contain water as a water of crystallisation.

D. Optical isomerism occurs mainly in compounds that are mirror images of each other.
cis $[CrCl_2(ox)_2]^{3+}$ is chiral compound, hence shows optical isomerism.

20 The correct pair(s) of the ambident nucleophiles is(are)

A. AgCN/KCN
B. *R*COOAg/*R*COOK
C. $AgNO_2/KNO_2$
D. AgI/KI **[2021, 17 March Shift-II]**

(a) B and C (b) Only A
(c) A and C (d) Only B

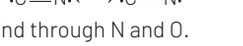
Ans. ***(c)***

The correct pair(s) of ambident nucleophile are (A) KCN and AgCN and (C) $AgNO_2$ and KNO_2.

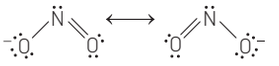
Ambident nucleophiles have the ability to bind the central atom *via* the two different atoms.

Structure are as follows:

^-CN can bind through C and N atoms.



NO_2^- can bind through N and O.

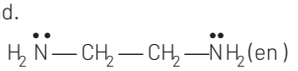


21 The equivalents of ethylene diamine required to replace the neutral ligands from the coordination sphere of the *trans*-complex of $COCl_3 \cdot 4NH_3$ is ..... (Round off to the nearest integer). **[2021, 16 March Shift-I]**

Ans. ***(2)***

$[Co(NH_3)_4Cl_2]Cl + 2en \longrightarrow [Co(en)_2Cl_2] + 4NH_3$

NH_3 is the neutral monodentate ligand. Ethylene diamine is a neutral didentate ligand.



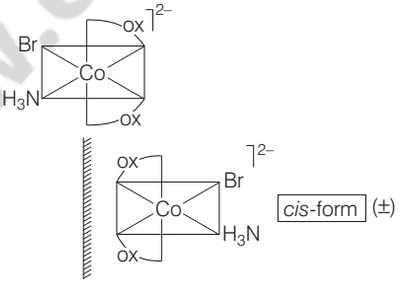
So, two ethylene diamine are equivalent to four 'NH_3' ligand.

22 The number of stereoisomers possible for $[Co(ox)_2(Br)(NH_3)]^{2-}$ is ..... [ox = oxalate].

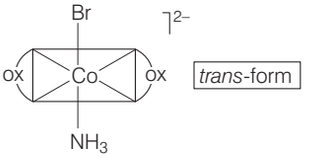
[2021, 26 Feb Shift-II]

Ans. ***(3)***

The coordination compound $[Co^{III}(ox)_2(Br)(NH_3)]^{2-}$ of general formula $[M(A—A)_2BC]$ can show both geometrical and optical isomerism (stereoisomerism).



The *cis*-form produces non-superimposable mirror images, i.e. enantiomeric pairs (optically active)



The *trans*-form is optically inactive.

So, total number of stereoisomers possible = *cis* (±) + *trans* = 3

23 Given below are two statements.

Statement I The identification of Ni^{2+} is carried out by dimethyl glyoxime in the presence of NH_4OH.

Statement II The dimethyl glyoxime is a bidentate neutral ligand.

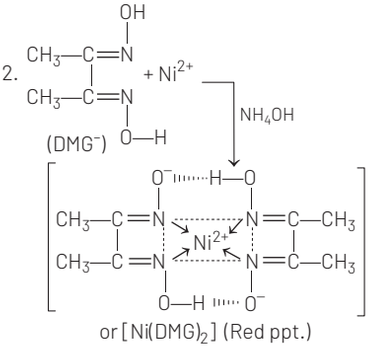
In the light of the above statements, choose the correct answer from the options given below. **[2021, 25 Feb Shift-II]**

(a) Both statements I and II are true.
(b) Both statements I and II are false.
(c) Statement I is true but statement II is false.
(d) Statement I is false but statement II is true.

Ans. ***(a)***

Both statements are true. Dimethyl glyoxime (DMG) is a neutral bidentate ligand (DMG^-).

Ni^{2+} ion is identified with DMG in presence of NH_4OH to give a red ppt. Its reaction is as follows.



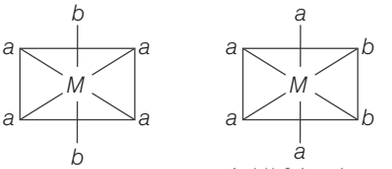
or $[Ni(DMG)_2]$ (Red ppt.)

24 The one that is not expected to show isomerism is **[2020, 2 Sep Shift-II]**

(a) $[Ni(NH_3)_4(H_2O)_2]^{2+}$
(b) $[Ni(en)_3]^{2+}$
(c) $[Ni(NH_3)_2Cl_2]$
(d) $[Pt(NH_3)_2Cl_2]$

Ans. ***(c)***

$[Ni(NH_3)_4(H_2O)]^{2+}$ of formula Ma_4b_2 shows geometrical isomerism.



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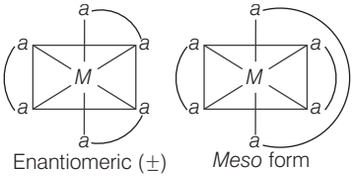
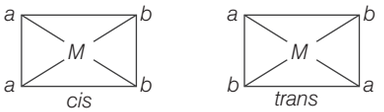
$[Ni(en)_3]^{2+}$ of formula, $M(a-a)_3$ shows optical isomerism.



In $[Ni(NH_3)_2Cl_2]$, Ni(II) is sp^3-hybridised. So, the complex has tetrahedral geometry. So, stereoisomers (geometrical and optical) as well as structural isomerism will not be shown by the complex. In $[Pt(NH_3)_2Cl_2]$, Pt(II) is dsp^2-hybridised and the complex has square planar geometry of general formula, Ma_2b_2 which shown geometrical isomerism.

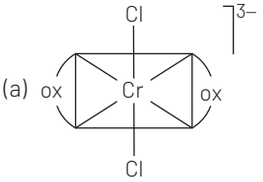


25 The complex that can show optical activity is **[2020, 3 Sep Shift-I]**

(a) *trans*-$[Cr(Cl_2)(ox)_2]^{3-}$
(b) *trans*-$[Fe(NH_3)_2(CN)_4]^-$
(c) *cis*-$[Fe(NH_3)_2(CN)_4]^-$
(d) *cis*-$[CrCl_2(ox)_2]^{3-}$ (ox = oxalate)

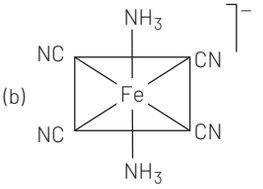
Ans. ***(d)***

(a)



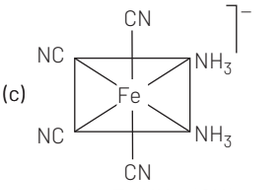
⇒ *trans*-$[Cr(Cl_2)(ox)_2]^{3-}$ will give super-imposable mirror image. (Optically inactive)

(b)



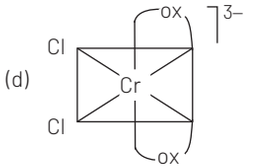
⇒ *trans*-$[Fe(NH_3)_2(CN)_4]^-$ will also give super-impoable mirror image. (Optically inactive)

(c)



⇒ *cis*-$[Fe(NH_3)_2(CN)_4]^-$ has also plane of symmetry and it is also optically inactive.

(d)



⇒ *cis*-$[CrCl_2(ox)_2]^{3-}$ will give non-supper imposable mirror image.
So, it is optically active.

So, option (d) is correct.

26 Complex (*A*) has a composition of $H_{12}O_6Cl_3Cr$. If the complex on treatment with conc. H_2SO_4 loses 13.5% of its original mass, the correct molecular formula of (*A*) is[Given : atomic mass of Cr = 52 amu and Cl = 35 amu] **[2020, 3 Sep Shift-II]**

(a) $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$
(b) $[Cr(H_2O)_6]Cl_3$
(c) $[Cr(H_2O)_5Cl]Cl_2\cdot H_2O$
(d) $[Cr(H_2O)_3Cl_3]\cdot 3H_2O$

Ans. ***(a)***

Complex (*A*) = $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$

Generally, conc. H_2SO_4 can act as oxidising agent as well as dehydrating agent. Here, H_2SO_4 act as dehydrating agent.

Molar mass of complex = 266.5 g/mol

On reaction with conc. H_2SO_4 the mass by complex = $\frac{13.5}{100}\times 266.5 = 35.9775 \approx 36$ g

It means that 2 moles of H_2O are present in complex.

[∵ Molar mass of H_2O = 18 g/mol]

Then, formula of complex is

$[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$

27 The number of isomers possible for $[Pt(en)(NO_2)_2]$ is **[2020, 4 Sep Shift-I]**

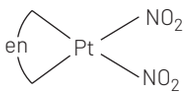
(a) 3 (b) 2 (c) 4 (d) 1

Ans. ***(a)***

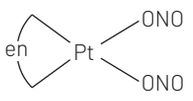
Total number of possible isomers for $[Pt(en)(NO_2)_2]$ are 3.

NO_2 — ambidentate ligand, en— bidentate ligand and coordination number is 4.

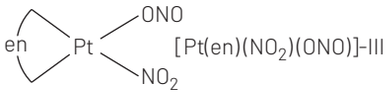
Structures are as follows :



$[Pt(en)(NO_2)_2]$-I



$[Pt(en)(ONO)_2]$-II

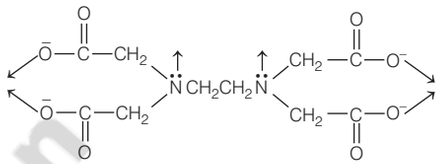


$[Pt(en)(NO_2)(ONO)]$-III

28 The total number of coordination sites in ethylenediaminetetraacetate $[EDTA^{4-}]$ is ... . **[2020, 5 Sep Shift-I]**

Ans. ***(6)***

$EDTA^{4-}$ is ethylenediaminetetraacetate anion. It is a polyprotic acid containing four carboxylic acid groups and two amine groups with lone-pair electrons that chelate calcium and several other metal ions, it has six coordination sites.



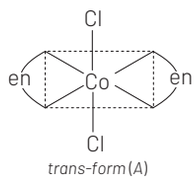
It is a hexadentate ligand.

29 Consider the complex ions, *trans*-$[Co(en)_2Cl_2]^+$ (*A*) and *cis*-$[Co(en)_2Cl_2]^+$ (*B*). The correct statement regarding them is **[2020, 5 Sep Shift-II]**

(a) both (*A*) and (*B*) cannot be optically active
(b) (*A*) can be optically active, but (*B*) cannot be optically active
(c) both (*A*) and (*B*) can be optically active
(d) (*A*) cannot be optically active, but (*B*) can be optically active

Ans. ***(d)***

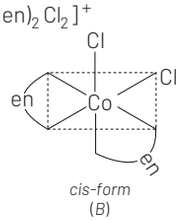
(*A*) *trans*-$[Co(en)_2Cl_2]^+$



trans-form (*A*)

(*A*) is a *trans*-form and shows plane of symmetry which makes it optically inactive (not optically active).

(*B*) *cis*-$[Co(en)_2Cl_2]^+$



cis-form (*B*)

cis-form does not contain any plane of symmetry. So that, the compound (*B*) is optically active.

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30 The theory that can completely/ properly explain the nature of bonding in $[Ni(CO)_4]$ is : **[2020, 7 Jan Shift-I]**

(a) Werner's theory
(b) Crystal field theory
(c) Valence bond theory
(d) Molecular orbital theory

Ans. ***(d)***

Bonding in metal carbonyls like $[Ni(CO)_4]$ can't be properly explained by Werner's theory, valence bond theory or crystal field theory. The concept of synergic bonding based on molecular orbital theory is used to explain their bonding. In $Ni(CO)_4$, backbonding involving filled *d*-orbitals of Ni and antibonding π^* orbitals of carbon monoxide is part of synergic bonding.

Thus, the nature of bonding in $Ni(CO)_4$ is completely explained by molecular orbital theory.

31 The IUPAC name of the complex $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ is **[2020, 7 Jan Shift-I]**

(a) diammine (methanamine) chlorido platinum (II) chloride
(b) diamminechlorido (methanamine) platinum (II) chloride
(c) diamminechlorido (aminomethane) platinum (II) chloride
(d) bisammine (methanamine) chlorido platinum (II) chloride

Ans. ***(b)***

The given compound has a cationic part $[Pt(NH_3)_2Cl(NH_2CH_3)]^+$ and anionic part Cl^-. Cationic part is a complex, so its name starts with ligands in alphabetical order followed by metal (with oxidation number in bracket). Ligands are NH_3 (ammine), Cl^- (chloride) and CH_3NH_2 (methanamine). For two NH_3, diammine is used.

'Methanamine' is written inside paranthesis or bracket because it is itself a composite name. (For such ligands, when two of them are present, '*bis*' is used instead of 'di'). Oxidation number of Pt in the complex is +2.

∴ The correct IUPAC name is diammine-chlorido (methanamine) platinum (II) chloride.

32 The number of possible optical isomers for the complexes MA_2B_2 with sp^3 and dsp^2 hybridised metal atom, respectively, is

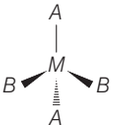
Note : *A* and *B* are unidentate neutral and unidentate monoanionic ligands, respectively. **[2020, 7 Jan Shift-II]**

(a) 0 and 0 (b) 0 and 1
(c) 2 and 2 (d) 0 and 2

Ans. ***(a)***

Optical isomerism is possible only in chiral molecules. A structure is chiral, if its mirror image is non-superimposable and therefore, it should not have a centre of symmetry or plane of symmetry.

An MA_2B_2 complex of sp^3-hybridised metal (*M*) has tetrahedral geometry.



There are clearly many planes of symmetry in the structure and the structure is

superimposable on its mirror image.

∴ It has no optical isomers.

An MA_2B_2 complex of dsp^2-hybridised metal (*M*) has square planar geometry.

There are two geometrical isomers *cis* and *trans*.

But, since they are planar and therefore they always have a plane of symmetry.

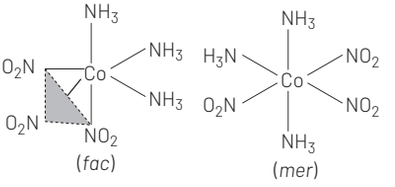
∴ No optical isomerism also.

33 The complex that can show *fac*- and *mer*-isomers is : **[2020, 8 Jan Shift-I]**

(a) $[Pt(NH_3)_2Cl_2]$
(b) $[Co(NH_3)_3(NO_2)_3]$
(c) $[Co(NH_3)_4Cl_2]^+$
(d) $[CoCl_2(en)_2]$

Ans. ***(b)***

Octahedral coordination entities of the type $[Ma_3b_3]$ shows geometical isomers: *fac* and *mer* isomers. Among the given complexes, the complex with general formula $[Ma_3b_3]$ is $[Co(NH_3)_3(NO_2)_3]$. Thus, it can show *fac* and *mer* isomers as follows:



34 Among (A) - (D), the complexes that can display geometrical isomerism are

(A) $[Pt(NH_3)_3Cl]^+$
(B) $[Pt(NH_3)Cl_5]^-$
(C) $[Pt(NH_3)_2Cl(NO_2)]$
(D) $[Pt(NH_3)_4ClBr]^{2+}$

[2020, 8 Jan Shift-II]

(a) (D) and (A) (b) (C) and (D)
(c) (A) and (B) (d) (B) and (C)

Ans. ***(b)***

(A) $[Pt(NH_3)_3Cl]^+$: No geometrical isomerism

(B) $[Pt(NH_3)Cl_5]^-$: No geometrical isomerism

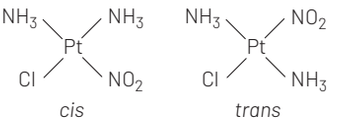
(C) $[Pt(NH_3)_2Cl(NO_2)]$: Has 2 geometrical isomers

(D) $[Pt(NH_3)_4ClBr]^{2+}$: exhibit geometrical isomerism.

All Pt^{2+} complexes with coordination number equals to 4 are square planar.

∴ The two NH_3 ligands could arrange in *cis* or *trans* positions.

∴ There are two geometrical isomers.

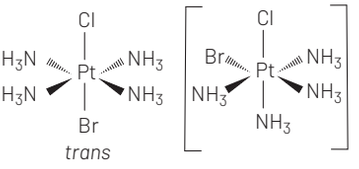


(D)) $[Pt(NH_3)_4ClBr]$: Two geometrical isomers Coordination number = 6

∴ Octahedral geometry

Cl and Br can be *cis* or *trans*

∴ 2 geometrical isomers



35 Complex *X* of composition $Cr(H_2O)_6Cl_n$ has a spin only magnetic moment of 3.83BM. It reacts with $AgNO_3$ and shows geometrical isomerism. The IUPAC nomenclature of *X* is **[2020, 9 Jan Shift-II]**

(a) tetraaquadichlorido chromium (IV) chloride dihydrate
(b) hexaaqua chromium (III) chloride
(c) dichloridotetraaqua - chromium (IV) chloride dihydrate
(d) tetraaquadichlorido - chromium (III) chloride dihydrate

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Ans. ***(d)***

$Cr(H_2O)_6Cl_n$ (*X*)

Spin only magnetic moment = 3.83 BM

$\therefore \quad \sqrt{n(n+2)} = 3.83$

$\Rightarrow$ *n*(number of unpaired electrons) = 3

(Note : the '*n*' used in the formula $Cr(H_2O)_6Cl_n$ is not this '*n*').

To have 3 unpaired electrons, Cr must be in +3 oxidation state. $Cr^{3+} = d^3$,

$\therefore$ 3 unpaired electrons are present.

$\therefore$ Chemical formula = $Cr(H_2O)_6Cl_3$

(*n* in the formula $Cr(H_2O)_6Cl_n$ is also = 3, because Cr is +3, $3Cl^-$ must be there).

To show geometrical isomerism, at least two different types of ligands must be there and at least two ligand of each type should be present.

$\therefore$ It must be $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ or $[Cr(H_2O)_3Cl_3]\cdot 3H_2O$

But it is also given that, the complex reacts with $AgNO_3$.

$\therefore$ At least one Cl^- ion must be outside coordination sphere.

$\therefore$ It must be $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

IUPAC name :

Tetraaquadichloridochromium (III) chloride dihydrate.

36 The isomer (s) of $[Co(NH_3)_4Cl_2]$ that has/have a Cl—Co—Cl angle of 90°, is/are **[2020, 9 Jan Shift-II]**

(a) *cis* and *trans*

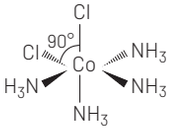
(b) meridional and *trans*

(c) *cis* only

(d) *trans* only

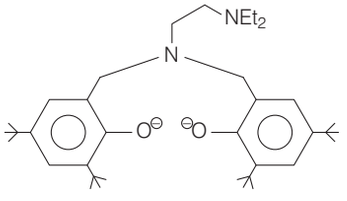
Ans. ***(c)***

The isomers of $[Co(NH_3)_4Cl_2]$ that have a Cl—Co—Cl angle of 90° is *cis* only.



trans isomer has Cl—Co—Cl angle of 180°.

37 The following ligand is



[2019, 8 April Shift-I]

(a) hexadentate (b) tetradentate

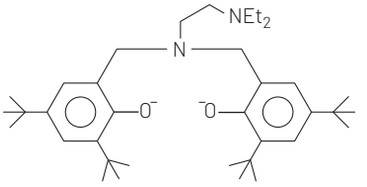
(c) bidentate (d) tridentate

Ans. ***(b)***

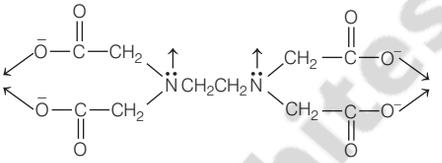
Key Idea Denticity of ligand is defined as donor sites or number of ligating groups.

The given ligand is tetradentate. It contains four donor atoms. It can bind through two nitrogen and two oxygen atom to the central metal ion.

Ligand bound to the central atom or ion through coordinate bond in the coordination entity. It act as a Lewis base. The attacking site of the given ligand is given in bold.



38 The species that can have a *trans*-isomer is (en = ethane -1, 2-diamine, ox = oxalate) **[2019, 10 April Shift-I]**



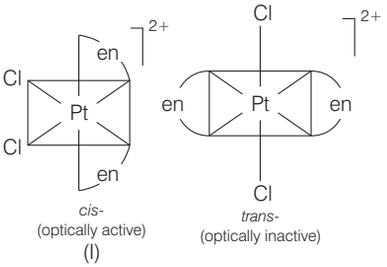
(a) $[Pt(en)Cl_2]$ (b) $[Cr(en)_2(ox)]^+$

(c) $[Pt(en)_2Cl_2]^{2+}$ (d) $[Zn(en)Cl_2]$

Ans. ***(c)***

Key Idea Square planar complexes of general formulae : $[M(a-a)b_2]$ and $[M(a-a)(b-b)]$ do not show geometrical isomerism. Whereas, an octahedral complex of general formula $[M(a-a)_2b_2]$ can show geometrical (*cis-trans*) isomerism.

$[Pt(en)_2(Cl_2)]^{2+}$ with formula $[M(a-a)_2b_2]$ will show geometrical isomerism as follows:



39 The coordination numbers of Co and Al in $[CoCl(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$, respectively, are (en = ethane-1, 2-diamine) **[2019, 12 April Shift-II]**

(a) 5 and 3 (b) 3 and 3

(c) 6 and 6 (d) 5 and 5

Ans. ***(d)***

Key Idea The total number of ligands to which the metal is directly attached is called coordination number.

The coordination numbers of Co and Al in $[Co(Cl)(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$ are 5 and 6 respectively.

In first complex, 'en' is a didentate ligand and 'Cl' is a unidentate ligand.

$[Co(Cl)(en)_2]Cl$, coordination number

$= 1 + 2 \times 2 = 1 + 4 \Rightarrow 5$

So, the coordination number is 5.

For $K_3[Al(C_2O_4)_3]$, '$C_2O_4^{2-}$' is a didentate ligand.

Coordination number = $3 \times 2 = 6$.

Hence, coordination number is 6.

40 The total number of isomers for a square planar complex $[M(F)(Cl)(SCN)(NO_2)]$ is

(a) 12 (b) 16

(c) 4 (d) 8

[2019, 10 Jan Shift-I]

Ans. ***(a)***

A square planar complex of general formula, M_{abcd} gives three geometrical isomers only.

Let, $a = F^-$, $b = Cl^-$, $c = S\,CN^-$, $d = NO_2^-$

SCN^- and NO_2^- are ambidentate ligands and they also show linkage isomerism (structural). Considering both linkage and geometrical isomerism.

Total number of possible isomers given by the complex, $= 3 \times (2 + 2) = 12$

41 A reaction of cobalt (III) chloride and ethylene diamine in a 1:2 mole ratio generates two isomeric products *A* (violet coloured) and *B* (green coloured). *A* can show optical activity, but *B* is optically inactive. What type of isomers does *A* and *B* represent ? **[2019, 10 Jan Shift-II]**

(a) Ionisation isomers

(b) Coordination isomers

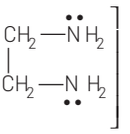
(c) Geometrical isomers

(d) Linkage isomers

Ans. ***(c)***

According to the situation given in question, reactions are as follows:

$$\overset{III}{Co}Cl_3 + 2en \longrightarrow [\overset{III}{Co}(en)_2Cl_2]Cl$$

en = ethylene-1, 2-diamine, 

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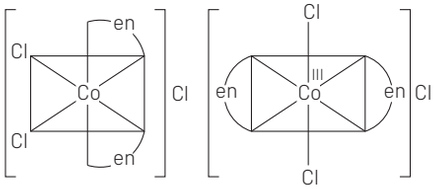


'A' Optically active (*cis-form*) (Violet) | 'B' Optically inactive (*trans-form*) (Green)

42 The coordination number of Th in $K_4[Th(C_2O_4)_4(OH_2)_2]$ is ($C_2O_4^{2-}$ = Oxalato)

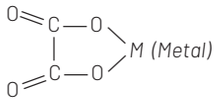
(a) 14 (b) 10
(c) 8 (d) 6

[2019, 11 Jan Shift-II]

Ans. ***(b)***

Coordination number is defined as the total number of ligands to which the metal is directly attached.

Here, $C_2O_4^{2-}$ is a bidentate ligand,



and H_2O is a monodentate ligand,

$H_2\ddot{O}: \longrightarrow M$

So, total number of sites offered by $C_2O_4^{2-}$ and H_2O ligands around Th(IV) = Coordination number of Th(IV)

$= 4 \times 2$(by $C_2O_4^{2-}$) $+ 2 \times 1$(by H_2O) $= 10$

43 The oxidation states of Cr, in $[Cr(H_2O)_6]Cl_3$, $[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$ respectively are **[JEE Main 2018]**

(a) +3, +4 and +6 (b) +3, +2 and +4
(c) +3, 0 and +6 (d) +3, 0 and +4

Ans. ***(b)***

Let the oxidation state of Cr in all cases is 'x'

(i) Oxidation state of Cr in $[Cr(H_2O)_6]Cl_3$

$x + (0 \times 6) + (-1 \times 3) = 0$

or $x + 0 - 3 = 0$ or $x = +3$

(ii) Oxidation state of Cr in $[Cr(C_6H_6)_2]$

$x + (2 \times 0) = 0$ or $x = 0$

(iii) Oxidation state of Cr in $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$

$1 \times 2 + x + (-1 \times 2) + (-2 \times 2) + (-2) + 0 = 0$

or $2 + x - 2 - 4 - 2 = 0$

or $x - 6 = 0$

hence $x = +6$

Thus, +3, 0 and +6 is the answer.

44 Consider the following reaction and statements : **[JEE Main 2018]**

$[Co(NH_3)_4Br_2]^+ + Br^- \longrightarrow [Co(NH_3)_3Br_3] + NH_3$

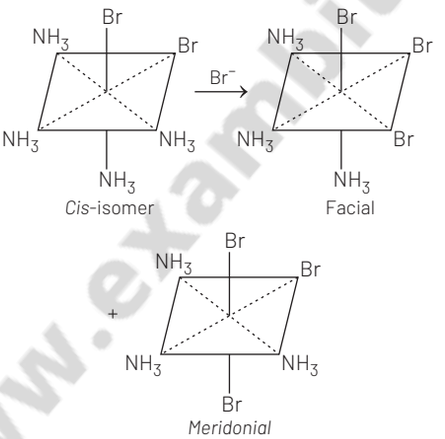
I. Two isomers are produces if the reactant complex ion is a *cis*-isomer.
II. Two isomers are produced if the reactant complex ion is a *trans*-isomer.
III. Only one isomer is produced if the reactant complex ion is a *trans*-isomer.
IV. Only one isomer is produced if the reactant complex ion is a *cis*-isomer.

The correct statements are

(a) (I) and (II)
(b) (I) and (III)
(c) (III) and (IV)
(d) (II) and (IV)

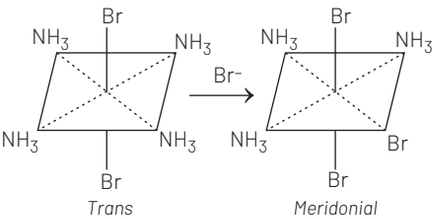
Ans. ***(b)***

If the reactant is *cis* isomer than following reaction takes place.



i.e. two isomers are produced.

If the reactant is *trans* isomer than following reaction takes place.



i.e. only 1 isomer is produced. Thus, statement (I) and (III) are correct resulting to option (b) as the correct answer.

45 A solution containing 2.675 g of $CoCl_3 \cdot 6NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is (Atomic mass of Ag = 108 u) **[AIEEE 2010]**

(a) $[Co(NH_3)_6]Cl_3$
(b) $[CoCl_2(NH_3)_4]Cl$
(c) $[CoCl_3(NH_3)_3]$
(d) $[CoCl(NH_3)_5]Cl_2$

Ans. ***(a)***

Mole of $CoCl_3 \cdot 6NH_3 = \frac{2.675}{267.5} = 0.01$ mol

$AgNO_3(aq) + Cl^-(aq) \longrightarrow AgCl\downarrow$(white) $+ NO_3^-(aq)$

Moles of AgCl $= \frac{4.78}{143.5} = 0.03$ mol

0.01 mol $CoCl_3 \cdot 6NH_3$ gives = 0.03 mol AgCl

$\therefore$ 1 mol $CoCl_3 \cdot 6NH_3$ ionises to give = 3 mol Cl^-

Hence, the formula of compound is $[Co(NH_3)_6]Cl_3$.

46 On treatment of 100 mL of 0.1 M solution of $CoCl_3 . 6H_2O$ with excess of $AgNO_3$; 1.2×10^{22} ions are precipitated. The complex is **[JEE Main 2017]**

(a) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$
(b) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$
(c) $[Co(H_2O)_6]Cl_3$
(d) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$

Ans. ***(d)***

Molarity (M) $= \frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$

$\therefore$ Number of moles of complex

$= \frac{\text{Molarity} \times \text{volume (in mL)}}{1000}$

$= \frac{0.1 \times 100}{1000} = 0.01$ mole

Number of moles of ions precipitate

$= \frac{1.2 \times 10^{22}}{6.02 \times 10^{23}} = 0.02$ moles

$\therefore$ Number of Cl^- present in ionisation sphere

$= \frac{\text{Number of moles of ions precipitated}}{\text{Number of moles of complex}}$

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$$= \frac{0.02}{0.01} = 2$$

$\therefore$ 2 Cl^- are present outside the square brackets, i.e. in ionisation sphere. Thus, the formula of complex is $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$.

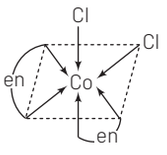
47 The pair having the same magnetic moment is
[at. no. Cr = 24, Mn = 25, Fe = 26 and Co = 27] **[JEE Main 2016]**
(a) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$
(b) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$
(c) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$
(d) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

Ans. ***(a)***

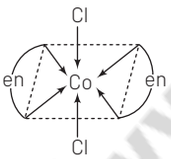
Complex ion	Electronic configuration of metal ion	Number of unpaired electrons (n)
$[Cr(H_2O)_6]^{2+}$	Cr^{2+}; $[Ar]3d^4$	⇅ 1 1 1 1 ; 4
$[Fe(H_2O)_6]^{2+}$	Fe^{2+}; $[Ar]3d^6$	1 1 1 1 1 ; 5
$[Mn(H_2O)_6]^{2+}$	Mn^{2+}; $[Ar]3d^5$	⇅ ⇅ 1 1 1 ; 3
$[CoCl_4]^{2-}$	Co^{2+}; $[Ar]3d^7$	1 1 1 1 ; 4

48 Which one of the following complexes shows optical isomerism? **[JEE Main 2016]**
(a) *cis* $[Co(en)_2Cl_2]Cl$
(b) *trans* $[Co(en)_2Cl_2]Cl$
(c) $[Co(NH_3)_4Cl_2]Cl$
(d) $[Co(NH_3)_3Cl_3]$

Ans. ***(a)***

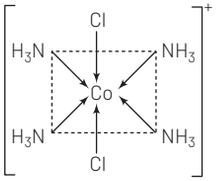


cis-$[Co(en)_2Cl_2]Cl$
(optically active)

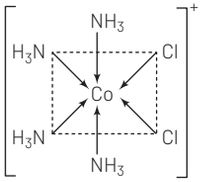


trans-$[Co(en)_2Cl_2]Cl$
(optically inactive due to plane of symmetry)

$[Co(NH_3)_4Cl_2]Cl$ can exist in both *cis* and *trans* forms that are given below:

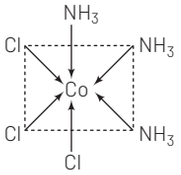


trans-$[Co(NH_3)_4Cl_2]Cl$
(optically inactive)

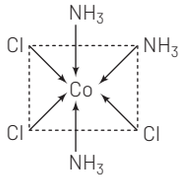


cis-$[Co(NH_3)_4Cl_2]Cl$
(optically inactive)

$[Co(NH_3)_3Cl_3]$ exists in *fac* and *mer*-isomeric forms and both are optically inactive.



fac-isomer
(optically inactive)



mer-isomer
(optically inactive)

49 The equation which is balanced and represents the correct product(s) is **[JEE Main 2013]**
(a) $Li_2O + 2KCl \longrightarrow 2LiCl + K_2O$
(b) $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$
(c) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$
(d) $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$

Ans. ***(b)***

(a) $Li_2O + 2KCl \longrightarrow 2LiCl + K_2O$
The above equation is incorrect because K_2O, a stronger base cannot be generated by a weaker base, Li_2O.

(b) $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$
The above equation is correct because amine complexes decomposes under acidic medium. Thus, the complex $[CoCl(NH_3)_5]$ decomposes under acidic conditions to give ammonium ions.

(c) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$
The above equation is incorrect because the product formed would be $[Mg(EDTA)]^{2-}$.

(d) $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$
The above equation is incorrect. Thus, the correct equation is
$2KCN + CuSO_4 \longrightarrow K_2SO_4 + Cu + (CN)_2$
(Cyanogen gas)

50 Which of the following complex species is not expected to exhibit optical isomerism? **[JEE Main 2013]**
(a) $[Co(en)_3]^{3+}$ (b) $[Co(en)_2Cl_2]^+$
(c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(en)(NH_3)Cl_2]^+$

Ans. ***(c)***

Optical isomerism is exhibited by only those complexes which lacks elements of symmetry.
$[Co(NH_3)_3Cl_3]$ shows facial as well as meridional isomerism. But both the forms contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

51 Which among the following will be named as dibromidobis-(ethylenediamine) chromium (III) bromide? **[AIEEE 2012]**
(a) $[Cr(en)_3]Br_3$ (b) $[Cr(en)_2Br_2]Br$
(c) $[Cr(en)Br_4]^-$ (d) $[Cr(en)Br_2]Br$

Ans. ***(b)***

Two Br, two (en) and one Cr are parts of complex.
Charge on the complex is
2(Br) = −2
2(en) = 0
1(Cr) = +3
} = +1
Thus, complex ion is $[Cr(en)_2Br_2]^+$.
Since, anion is bromide thus, complex is $[Cr(en)_2Br_2]Br$.

52 Among the ligands NH_3, en, CN^- and CO, the correct order of their increasing field strength, is **[AIEEE 2011]**
(a) $CO < NH_3 < en < CN^-$
(b) $NH_3 < en < CN^- < CO$
(c) $CN^- < NH_3 < CO < en$
(d) $en < CN^- < NH_3 < CO$

Ans. ***(b)***

Based on spectrochemical series, ligands arranged in increasing order of crystal field strength are as
$NH_3 < en < CN^- < CO$

53 Which one of the following complex ions has geometrical isomers? **[AIEEE 2011]**
(a) $[Co(en)_3]^{3+}$
(b) $[Ni(NH_3)_5Br]^+$
(c) $[Co(NH_3)_2(en)_2]^{3+}$
(d) $[Cr(NH_3)_4(en)]^{3+}$

Ans. ***(c)***

	Complex	Isomerism shown
(a)	$[Co(en)_3]^{3+}$	Optical only
(b)	$[Ni(NH_3)_5Br]^+$	No geometrical isomer
(c)	$[Co(NH_3)_2(en)_2]^{3+}$	*Cis* and *trans*
(d)	$[Cr(NH_3)_4(en)]^{3+}$	No geometrical isomer

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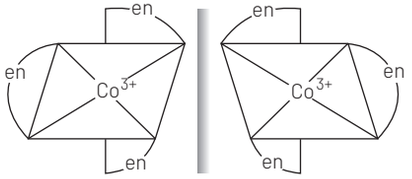
54 Which one of the following has an optical isomer? (en = ethylenediamine) **[AIEEE 2010]**

(a) $[Zn(en)(NH_3)_2]^{2+}$
(b) $[Co(en)_3]^{3+}$
(c) $[Co(H_2O)_4(en)]^{3+}$
(d) $[Zn(en)_2]^{2+}$

Ans. ***(b)***

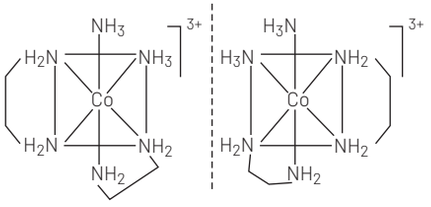
Complex $[Co(en)_3]^{3+}$ has no plane of symmetry and centre of symmetry. That's why, it is optically active.



55 Which of the following has an optical isomer? **[AIEEE 2009]**

(a) $[Co(NH_3)_3Cl]^+$
(b) $[Co(en)(NH_3)_2]^{2+}$
(c) $[Co(H_2O)_4(en)]^{3+}$
(d) $[Co(en)_2(NH_3)_2]^{3+}$

Ans. ***(d)***



56 Which of the following pairs represents linkage isomers? **[AIEEE 2009]**

(a) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
(b) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$
(c) $[Co(NH_3)_5]NO_3SO_4$ and $[Co(NH_3)_5SO_4]NO_3$
(d) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

Ans. ***(b)***

Linkage isomers are caused due to the presence of ambidentate ligands $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$ are linkage isomers due to SCN, an ambidentate ligand.

Thus, SCN can linked to Pd by both N as well as S through their lone pairs.

57 The coordination number and the oxidation state of the element '*E*' in the complex $[E(en)_2(C_2O_4)]NO_2$ (where (en) is ethylene diamine) are, respectively **[AIEEE 2008]**

(a) 6 and 2 (b) 4 and 2
(c) 4 and 3 (d) 6 and 3

Ans. ***(d)***

en, $CH_2—NH_2$ | $CH_2—NH_2$ is bidentate ligand

$C_2O_4^{2-}$ is also bidentate ligand.

Hence, coordination number of the element *E* in the given complete comes out to be 6.

The complex can be ionised as

$[E(en)_2(C_2O_4)]NO_2 \longrightarrow [E(en)_2(C_2O_4)]^+ NO_2^-$

Oxidation number $x + 0 + (-2) = +1$

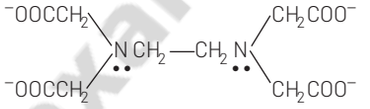
$\Rightarrow$ Oxidation number, $x = 3$

58 How many EDTA (ethylenediamine tetraacetic acid) molecules are required to make an octahedral complex with a Ca^{2+} ion? **[AIEEE 2006]**

(a) Six (b) Three
(c) One (d) Two

Ans. ***(c)***

EDTA (Ethylenediamine tetraacetic acid)



It is hexadentate (6 electron pairs).

That's why for octahedral complex, only one EDTA is required.

59 The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]Cl_2$ is **[AIEEE 2006]**

(a) nitrito-N-pentamminecobalt (III) chloride
(b) nitrito-N-pentamminecobalt (II) chloride
(c) pentammine nitrito-N-cobalt (II) chloride
(d) pentammine nitrito-N-cobalt (III) chloride

Ans. ***(d)***

The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]Cl_2$

Pentammine nitrito-N-cobalt (III) chloride

60 The IUPAC name of the coordination compound $K_3[Fe(CN)_6]$ is **[AIEEE 2005]**

(a) tripotassium hexacyanoiron (II)
(b) potassium hexacyanoiron (II)
(c) potassium hexacyanoferrate (III)
(d) potassium hexacyanoferrate (II)

Ans. ***(c)***

$K_3[Fe(CN)_6]$
Cation Anion

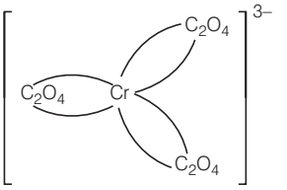
Oxidation state of Fe in anion = +3

Thus, it is potassium hexacyanoferrate (III).

61 Which of the following compounds shows optical isomerism ? **[AIEEE 2005]**

(a) $[Co(CN)_6]^{3-}$ (b) $[Cr(C_2O_4)_3]^{3-}$
(c) $[ZnCl_4]^{2-}$ (d) $[Cu(NH_3)_4]^{2+}$

Ans. ***(b)***



Mirror image is not superimposable, hence optical isomerism is possible.

62 Which one of the following has largest number of isomers? (*R* = alkyl group, en = ethylenediamine) **[AIEEE 2004]**

(a) $[Ru(NH_3)_4Cl_2]^+$
(b) $[Co(NH_3)_5Cl]^{2+}$
(c) $[Ir(PR_3)_2H(CO)]^{2+}$
(d) $[Co(en)_2Cl_2]^+$

Ans. ***(d)***

All the given compounds, exhibits geometrical (cis and trans isomers) but only cis isomer of $[CO(en)_2Cl_2]^+$ possess optical isomers (*d* and *l*) due to the presence of symmetrical didentate, en [ethylediamine].

63 One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl(*s*). The structure of the complex is **[AIEEE 2003]**

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(a) $[Co(NH_3)_5Cl]Cl_2$
(b) $[Co(NH_3)_3Cl_3]\cdot 2NH_3$
(c) $[Co(NH_3)_4Cl_2]Cl\cdot NH_3$
(d) $[Co(NH_3)_4Cl]Cl_2\cdot NH_3$

Ans. ***(a)***

The oxidation state of nickel is

$$\underset{\text{three ions}}{\underbrace{[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + 2Cl^-}}$$

64 In the coordination compound, $K_4[Ni(CN)_4]$ the oxidation state of nickel is **[AIEEE 2003]**

(a) −1 (b) 0 (c) +1 (d) +2

Ans. ***(b)***

The oxidation state of nickel is

$$K_4[Ni(CN)_4] \longrightarrow 4K^+ + [Ni(CN)_4]^{4-}$$
$$[Ni(CN)_4]^{4-} \longrightarrow x + (4\times -1) = -4$$
$$x - 4 = -4 \text{ or } x = 0$$

65 Type of isomerism shown by $[Cr(NH_3)_5NO_2]Cl_2$ is **[AIEEE 2002]**

(a) optical (b) ionisation
(c) geometrical (d) linkage

Ans. ***(d)***

$[Cr(NH_3)_5NO_2]Cl_2$(Pentamminenitrito chromium (III) chloride) exhibits linkage isomerism as $-NO_2$ is ambidentate ligand. Isomer is $[Cr(NH_3)_5ONO]Cl_2$.

66 A square planar complex is formed by the hybridisation of the following atomic orbitals **[AIEEE 2002]**

(a) s, p_x, p_y, p_z
(b) s, p_x, p_y, p_z, d
(c) d, s, p_x, p_y
(d) s, p_x, p_y, p_z, d, d

Ans. ***(c)***

A square planar geometry is the result of dsp^2 hybridisation where inner d sub-shell ($d_{x^2-y^2}$ orbital) participates.

TOPIC 2
Bonding in Coordination Compounds

67 The potassium ferrocyanide solution gives a prussian blue colour, when added to **[2021, 1 Sep Shift-II]**

(a) $CoCl_3$ (b) $FeCl_2$ (c) $CoCl_2$ (d) $FeCl_3$

Ans. ***(d)***

Potassium ferrocyanide solution $\{K_4[Fe(CN)_6]\}$ will give prussian blue colour when added to ferric chloride ($FeCl_3$) due to formation of iron (III)hexacyanoferrate (II).

$$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Iron (III) hexacyanido-ferrate (II)}\\ \text{(Prussian blue colour)}}}{Fe_4[Fe(CN)_6]_3}$$

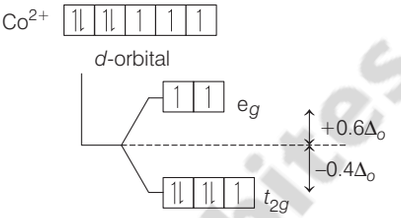
68 The crystal field stabilisation energy (CFSE) and magnetic moment (spin-only) of an octahedral aqua complex of a metal ion (M^+) are $-0.8\,\Delta_o$ and 3.87 BM, respectively.

Identify (M^{2+}). **[2021, 1 Sep Shift-II]**

(a) V^{3+} (b) Cr^{3+}
(c) Mn^{4+} (d) Co^{2+}

Ans. ***(d)***

The crystal field stabilisation energy (CFSE) and magnetic moment (spin-only) of Co^{2+} octahedral aqua complex are $-0.8\Delta_o$ and 3.87 BM respectively.



$$CFSE = [(e^- \text{ in } t_{2g})\times(-0.4) + (e^- \text{ in } e_g)\times 0.6]\,\Delta_o$$
$$= [5\times -0.4 + 2\times 0.6]\,\Delta_o$$
$$= -0.8\,\Delta_o$$

Magnetic moment (spin only) can be calculated as :

$$\mu = \sqrt{n(n+2)}$$

(where, μ = spin only magnetic moment and

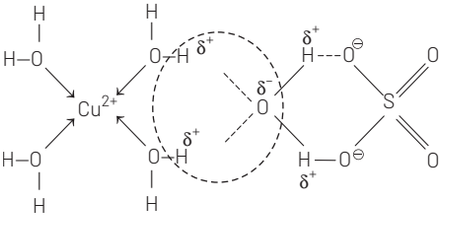
n = number of unpaired electrons = 3

$$= \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

69 The number of hydrogen bonded water molecule(s) associated with stoichiometry $CuSO_4\cdot 5H_2O$ is/are. **[2021, 31 Aug Shift-I]**

Ans. ***(1)***

The number of hydrogen bonded water molecule associated with stoichiometry $CuSO_4\cdot 5H_2O$ is 1.

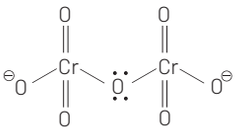


70 In the structure of the dichromate ion, there is a **[2021, 31 Aug Shift-I]**

(a) linear symmetrical Cr—O—Cr bond.
(b) non-linear symmetrical Cr—O—Cr bond.
(c) linear unsymmetrical Cr—O—Cr bond.
(d) non-linear unsymmetrical Cr—O—Cr bond.

Ans. ***(b)***

The structure of dichromate ion ($Cr_2O_7^{2-}$) contains a non-linear symmetrical Cr—O—Cr bond.



Hence, correct option is (b).

71 Acidic ferric chloride solution on treatment with excess of potassium ferrocyanide gives a prussian blue coloured colloidal species. It is **[2021. 27 Aug Shift-I]**

(a) $Fe_4[Fe(CN)_6]_3$
(b) $K_5Fe[Fe(CN)_6]_2$
(c) $HFe[Fe(CN)_6]$
(d) $KFe[Fe(CN)_6]$

Ans. ***(a)***

When a solution of ferric chloride is treated with potassium ferrocyanide solution, a prussian blue precipitate of ferric ferrocyanide is obtained.

$$\underset{\text{Ferric chloride}}{4FeCl_3} + \underset{\text{Potassium ferrocyanide}}{3K_4[Fe(CN)_6]} \longrightarrow \underset{\text{Ferric ferrocyanide}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

72 The overall stability constant of the complex ion $[Cu(NH_3)_4]^{2+}$ is 2.1×10^{13}. The overall dissociations constant is $y\times 10^{-14}$. Then, y is ..... . (Nearest integer) **[2021, 26 Aug Shift-II]**

Ans. ***(5)***

Given, $K_f = 2.1\times 10^{13}$

Dissociation constant

$$(K_d) = \frac{1}{K_f}$$
$$= 4.7\times 10^{-14}$$
$$\therefore \quad y = 4.7 \simeq 5.$$

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73 Arrange the following cobalt complexes in the order of increasing crystal field stabilisation energy (CFSE) value.

$[CoF_6]^{3-}$, $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$

(A) (B) (C) (D)

Choose the correct option.

[2021 26 Aug Shift-II]

(a) $A < B < C < D$ (b) $B < A < C < D$
(c) $B < C < D < A$ (d) $C < D < B < A$

Ans. ***(a)***

For the same central metal ion, the CFSE increases with increase in strength of the ligand. The order of strength of ligand is given by the spectrochemical series :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$

Thus, the order of CFSE of given complexes will be :

$[CoF_6]^{3-} < [Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(en)_3]^{3+}$.
(A) (B) (C) (D)

74 Which one of the following complexes is violet in colour?

[2021, 26 Aug Shift-I]

(a) $[Fe(CN)_6]^{4-}$
(b) $[Fe(SCN)_6]^{4-}$
(c) $Fe_4[Fe(CN_6)]_3.H_2O$
(d) $[Fe(CN)_5NOS]^{4-}$

Ans. ***(d)***

The complex $[Fe(CN)_5NOS]^{4-}$ is violet in colour. It is formed when sodium nitroprusside reacts with sulphide ion to give violet colour as follows

$S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}$
(Violet colour)

75 An aqueous solution of $NiCl_2$ was heated with excess sodium cyanide in presence of strong oxidising agent to form $[Ni(CN)_6]^{2-}$. The total change in number of unpaired electrons on metal centre is ..... .

[2021, 20 July Shift-II]

Ans. ***(2)***

$[Ni(CN)_6]^{2-}$

Oxidation state of Ni in $[Ni(CN)_6]^{2-}$

$\Rightarrow \quad x + 6(-1) = -2$

$x - 6 = -2$

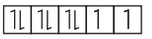
$\Rightarrow \quad x = +4$

$Ni^{+4} \rightarrow 3d^6 = t_{2g}^6, e_g^0$

(Presence of strong field)

Unpaired electron = 0

Similarly, $NiCl_2 \longrightarrow Ni^{2+}$

$d^8 =$ 

(Two unpaired electrons)

Number of unpaired electron in $NiCl_2$ and $[Ni(CN)_6]^{2-}$ are two and zero respectively.

Change in number of unpaired electrons $\Rightarrow$ 2 to 0.

Change = 2

76 The spin only magnetic moment value for the complex $[Co(CN)_6]^{4-}$ is ..... BM.

[Atomic number of Co = 27]

[2021, 20 July Shift-I]

Ans. ***(2)***

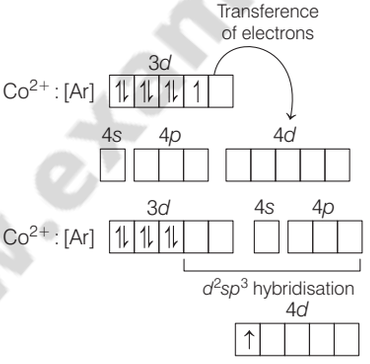
$[Co(CN)_6]^{4-}$

$x + 6 \times (-1) = -4$

where x, 6, -1 and -4 are the oxidation number of Co, number of CN ligands, charge on one CN and charge on complex.

$x = +2$, i.e. Co^{2+}

Electronic configuration of Co^{2+} : $[Ar]\,3d^7$ and CN^- is a strong field ligand which can pair electron of central atom.



It has one unpaired electron (n) in 4d-subshell.

So, spin only magnetic moment

$(\mu) = \sqrt{n(n+2)}$ BM

$= \sqrt{1(1+2)}$ BM $= \sqrt{3}$ BM

where, n = number of unpaired electrons

$\mu = \sqrt{3}$ BM $= 1.73$ BM

Nearest integer = 2

77 The secondary valency and the number of hydrogen bonded water molecules in $CuSO_4 \cdot 5H_2O$, respectively, are

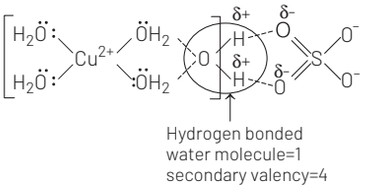
[2021, 18 March Shift-II]

(a) 6 and 4 (b) 4 and 1
(c) 6 and 5 (d) 5 and 1

Ans. ***(b)***

$CuSO_4 \cdot 5H_2O$ is blue vitriol, which is represented as $[Cu(H_2O)_4] \cdot H_2O \cdot SO_4$.

Here, secondary valencies are $4H_2O$ and $1H_2O$ molecule outside coordination sphere is involved in hydrogen bonding.



Hence, option (b) is correct.

78 The total number of unpaired electrons present in the complex $K_3[Cr(oxalate)_3]$ is ..... .

[2021, 18 March Shift-I]

Ans. ***(3)***

$K_3[Cr(ox)_3]$

Let, x be the oxidation state of Cr in $K_3[Cr(C_2O_4)_3]$. Since, the overall charge on the complex is 0, the sum of oxidation states of all elements in it should be equal to 0. Therefore,

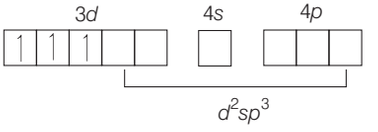
$+3 + x + 3(-2) = 0$ (oxalate is bidentate ligand and having -2 charge)

or, $x = +3$.

Hence, chromium is in +3 oxidation state.

$Cr \longrightarrow 3d^5 4s^1$ (ground state electronic configuration)

$Cr^{3+} \longrightarrow 3d^3 4s^0$ (Excited state)



CN = 6

$\therefore$ oxalate is weak field ligand

$\therefore$ 3 unpaired electron in d-orbital. The hybridisation of chromium in the complex is d^2sp^3.

79 On complete reaction of $FeCl_3$ with oxalic acid in aqueous solution containing KOH, resulted in the formation of product A. The secondary valency of Fe in the product A is ..... . (Round off to the nearest integer).

[2021, 17 March Shift-II]

Ans. ***(6)***

Secondary valency is equal to coordination number of central metal

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ion. In this reaction, central metal atom iron is attached with 3-oxalato ligand, and oxlaic acid it is a bidentate ligand i.e. have two donor sites. So, coordination number or secondary valency = 3 × 2 = 6

$$FeCl_3 + 3H_2C_2O_4 + 6KOH \longrightarrow \underset{(A)}{K_3[Fe(C_2O_4)_3]} + 3KCl + 6H_2O$$

Hence, product *A* have iron with secondary valency = 6

80 What is the spin-only magnetic moment value (BM) of a divalent metal ion with atomic number 25, in it's aqueous solution?

[2021, 17 March Shift-I]

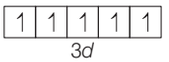
(a) 5.92 (b) 5.0
(c) zero (d) 5.26

Ans. ***(a)***

Atomic number 25 is for manganese (Mn).

Configuration of Mn = $[Ar]4s^2 3d^5$

In aqueous medium, $Mn^{2+} = [Ar]3d^5$



Total number of unpaired electrons = 5

μ (magnetic moment) = $\sqrt{n(n+2)}$ BM

where, n = number of unpaired electron

$\therefore \quad \mu = \sqrt{5(5+2)} = \sqrt{35}$ BM = 5.92 BM

81 Arrange the following metal complex/compounds in the increasing order of spin only magnetic moment. Presume all the three, high spin system.

(Atomic numbers Ce = 58, Gd = 64 and Eu = 63.)

A. $(NH_4)_2[Ce(NO_3)_6]$

B. $Gd(NO_3)_3$ and

C. $Eu(NO_3)_3$ **[2021, 16 March Shift-II]**

(a) (B) < (A) < (C) (b) (C) < (A) < (B)
(c) (A) < (B) < (C) (d) (A) < (C) < (B)

Ans. ***(d)***

(A) $_{58}Ce \longrightarrow [Xe]4f^2 5d^0 6s^2$

In complex

$Ce^{+4} \longrightarrow [Xe]4f^0 5d^0 6s^0$

There is no unpaired electron, so

$\mu_m = 0$ BM

(B) $_{64}Gd \longrightarrow [Xe]4f^7 5d^1 6s^2$

In complex,

$_{64}Gd^{2+} \longrightarrow [Xe]4f^7 5d^1$

There are 8 unpaired electrons.

$\therefore \mu_m = \sqrt{8(8+2)}$

$= \sqrt{80} = 8.94$ BM

(C) $_{63}Eu \longrightarrow [Xe]4f^9 5d^0 6s^0$

In complex

$_{63}Eu^{+3} \longrightarrow [Xe]4f^6 5d^0 6s^0$

contain six unpaired electrons.

So, $\mu_m = \sqrt{6(6+2)}$

$= \sqrt{48}$ BM

$= 6.93$ BM

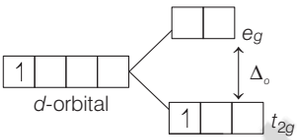
Hence, order of spin only magnetic moment $B > C > A$.

82 $[Ti(H_2O)_6]^{3+}$ absorbs light of wavelength 498 nm during a *d*-*d* transition. The octahedral splitting energy for the above complex is ..... $\times 10^{-9}$ J (Round off to the nearest intger). [$h = 6.626 \times 10^{-34}$ Js, $c = 3 \times 10^8$ ms^{-1}]

[2021, 16 March Shift-II]

Ans. ***(4)***

$[Ti(H_2O)_6]^{3+}$ is an octahedral complex.



For transition of electron from t_{2g} to e_g orbital, Δ_o amount of energy is required.

Given, $\lambda = 498$ nm $= 498 \times 10^{-9}$ m

$\Delta_o = hc/\lambda$

where, h = Planck's constant

c = speed of light

λ = wavelength of radiation

So, $\Delta_o = \dfrac{6.6 \times 10^{-34} \times 3 \times 10^8}{498 \times 10^{-9}}$

$= 3.98 \times 10^{-19}$ J

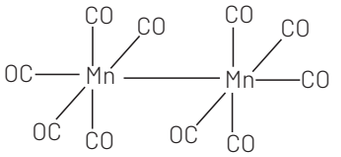
$= 4 \times 10^{-19}$

83 Number of bridging CO ligands in $[Mn_2(CO)_{10}]$ is ..... .

[2021, 26 Feb Shift-I]

Ans. ***(0)***

$[Mn_2(CO)_{10}]$ is a polynuclear metal carbonyl compound. It is decarboxyldimanganese (0) which is made up of two square pyramidal $Mn(CO)_5$ units joined by a Mn—Mn bond. The structure of $[Mn_2(CO)_{10}]$ is



Here, no CO ligand is a bridging ligand. So, number of bridging CO ligands in $[Mn_2(CO)_{10}]$ is 0 (zero).

84 In which of the following order the given complex ions are arranged correctly with respect to their decreasing spin only magnetic moment?

(i) $[FeF_6]^{3-}$ (ii) $[Co(NH_3)_6]^{3+}$
(iii) $[NiCl_4]^{2-}$ (iv) $[Cu(NH_3)_4]^{2+}$

[2021, 25 Feb Shift-II]

(a) (i) > (iii) > (iv) > (ii)
(b) (ii) > (iii) > (i) > (iv)
(c) (iii) > (iv) > (ii) > (i)
(d) (ii) > (i) > (iii) > (iv)

Ans. ***(a)***

Spin only magnetic moment,

$\mu = \sqrt{n(n+2)}$ BM

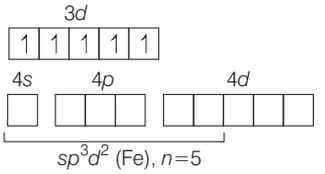
where, n = number of unpaired electrons and $\mu \propto n$.

(i) $[FeF_6]^{3-}$

$\Rightarrow Fe^{3+} = (3d^5) + 6 \times F^-$

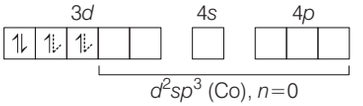
(weak field ligand).

Thus, pairing of electron does not take place.



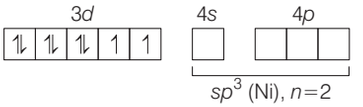
(ii) $[Co(NH_3)_6]^{3+} \Rightarrow$

$Co^{3+} = (3d^6) + 6 \times NH_3$ (strong field ligand). Thus, pairing of electron takes place.



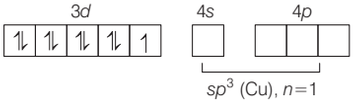
(iii) $[NiCl_4]^{2-} \Rightarrow Ni^{2+} = (3d^8) + 4 \times Cl^-$

(weak field ligand). Thus, pairing of electron takes place.



(iv) $[Cu(NH_3)_4]^{2+} \Rightarrow$

$Cu^{2+}(3d^9) + 4 \times NH_3$ (strong field ligand). Thus, pairing of electron takes place.



So, the decreasing order of μ is

$$\underset{(n=5)}{\mu_i} > \underset{(n=2)}{\mu_{iii}} > \underset{(n=1)}{\mu_{iv}} > \underset{(n=0)}{\mu_{ii}}$$

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85 The hybridisation and magnetic nature of $[Mn(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$, respectively are

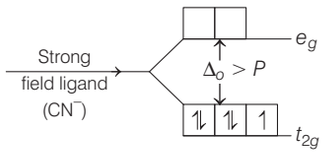
[2021, 25 Feb Shift-I]

(a) d^2sp^3 and paramagnetic
(b) sp^3d^2 and diamagnetic
(c) d^2sp^3 and diamagnetic
(d) sp^3d^2 and paramagnetic

Ans. ***(a)***

$[Mn(CN)_6]^{4-}$ In this complex, oxidation state of Mn is +2.

$Mn^{2+} = [Ar]\,3d^5$

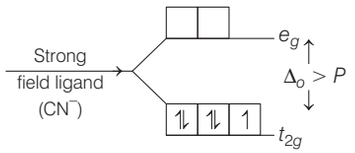


Hybridisation- d^2sp^3

Magnetic nature-Paramagnetic

$[Fe(CN)_6]^{-3}$

$Fe^{3+} = [Ar]\,3d^5$



Hybridisation- d^2sp^3

Magnetic nature-Paramagnetic

86 The calculated magnetic moments (spin only value) for species $[FeCl_4]^{2-}$, $[Co(C_2O_4)_3]^{3-}$ and MnO_4^{2-} respectively are

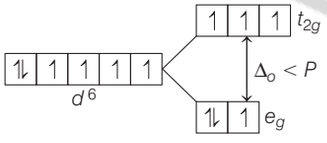
[2021, 24 Feb Shift-II]

(a) 5.82, 0 and 0 BM
(b) 4.90, 0 and 1.73 BM
(c) 5.92, 4.90 and 0 BM
(d) 4.90, 0 and 2.83 BM

Ans. ***(b)***

(i) $[FeCl_4]^{2-} \longrightarrow Fe^{2+} \longrightarrow [Ar]\,3d^6$

$\therefore$ Cl is weak field ligand so does not pairing occur



So, magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

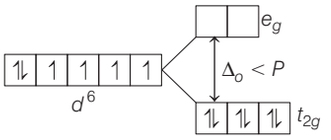
$= \sqrt{4(4+2)}$ BM

(n = Number of total unpaired $e^- = 4$)

$= \sqrt{24}$ BM = 4.90 BM

(ii) $[Co(C_2O_4)_3]^{3-} \longrightarrow Co^{3+} \longrightarrow [Ar]\,3d^6$

C_2O_4 is strong field ligand so pairing occur.



All electrons are paired, $n = 0$

hence, $\mu = 0$

(iii) $MnO_4^{2-} \rightarrow Mn^{+6} \rightarrow [Ar]3d^1$

$n = 1$

$= \sqrt{n(n+2)}$ BM $= \sqrt{1(1+2)}$ BM

$= \sqrt{3}$ BM = 1.73 BM

87 The stepwise formation of $[Cu(NH_3)_4]^{2+}$ is given below

$$Cu^{2+} + NH_3 \overset{K_1}{\rightleftharpoons} [Cu(NH_3)]^{2+}$$

$$[Cu(NH_3)]^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} [Cu(NH_3)_2]^{2+}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} [Cu(NH_3)]^{2+}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} [Cu(NH_3)_4]^{2+}$$

The value of stability constants K_1, K_2, K_3 and K_4 are 10^4, 1.58×10^3, 5×10^2 and 10^2 respectively. The overall equilibrium constants for dissociation of $[Cu(NH_3)]^{2+}$ is $x \times 10^{-12}$. The value of x is ..... . (Rounded off to the nearest integer)

[2021, 24 Feb Shift-I]

Ans. ***(1.26)***

Given, stability constant value, $k_1 = 10^4$

$k_2 = 1.58 \times 10^3$

$k_3 = 5 \times 10^2$

$k_4 = 10^2$

$$Cu^{2+} + NH_3 \overset{k_1}{\rightleftharpoons} [Cu(NH_3)]^{2+} \quad ...(i)$$

$$[Cu(NH_3)]^{2+} + NH_3 \overset{k_2}{\rightleftharpoons} [Cu(NH_3)_2]^{2+} \quad ...(ii)$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \overset{k_3}{\rightleftharpoons} [Cu(NH_3)_3]^{2+} \quad ...(iii)$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \overset{k_4}{\rightleftharpoons} [Cu(NH_3)_4]^{2+} \quad ...(iv)$$

$\vdots \qquad \vdots \qquad \vdots$

On adding Eqs. (i), (ii), (iii) and (iv), we get

$$Cu^{2+} + 4NH_3 \overset{k}{\rightleftharpoons} [Cu(NH_3)_4]^{2+}$$

$\therefore$ The overall reaction constant (k) or equilibrium constant for formation of $[Cu(NH_3)_4]^{2+}$ is

$k = k_1 \times k_2 \times k_3 \times k_4$

$k = 10^4 \times 1.58 \times 10^3 \times 5 \times 10^2 \times 10^2$

$k = 7.9 \times 10^{11}$

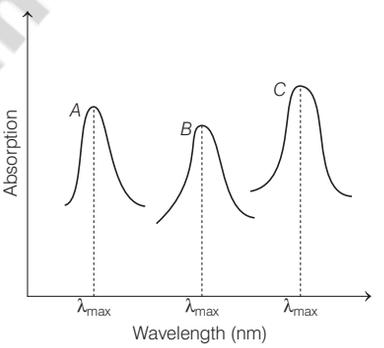
where, k = equilibrium constant for formation of $[Cu(NH_3)_4]^{2+}$

So, equilibrium constant k' for dissociation of $[Cu(NH_3)_4]^{2+}$ is $\frac{1}{k}$.

$$k' = \frac{1}{k} = \frac{1}{7.9 \times 10^{11}} = 1.26 \times 10^{-12}$$

Hence, $k' = x \times 10^{-12} \Rightarrow x = 1.26$

88 Simplified absorption spectra of three complexes [(i), (ii) and (iii)] of M^{n+} ion are provided below; their λ_{max} values are marked as *A*, *B* and *C* respectively. The correct match between the complexes and their λ_{max} values is



[2020, 2 Sep Shift-II]

(i) $[M(NCS)_6]^{(-6+n)}$
(ii) $[MF_6]^{(-6+n)}$
(iii) $[M(NH_3)_6]^{n+}$
(a) *A*-(iii), *B*-(i), *C*-(ii)
(b) *A*-(ii), *B*-(i), *C*-(iii)
(c) *A*-(ii), *B*-(iii), *C*-(i)
(d) *A*-(i), *B*-(ii), *C*-(iii)

Ans. ***(a)***

Here, same metal ion, M^{n+} form three homoleptic octahedral complexes (i), (ii) and (iii) on separate combination with three mono-dentate ligands–$\bar{\bar{N}}CS$, $\bar{\bar{F}}$ and NH_3 respectively.

So, we have to compare their CFSE (Δ_0) as well as wavelength (λ) values, where

$$\Delta E(CFSE) = \frac{hc}{\lambda} \text{ or, } \Delta_0 \propto \frac{1}{\lambda}$$

Again, Δ_0 value will depend on power of ligand as placed in spectrochemical series.

Power of ligand $\propto \Delta_0 \propto \frac{1}{\lambda}$,

$$F^- < NCS^- < NH_3, \bar{F} > N\bar{\bar{C}}S > NH_3$$

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$\longrightarrow$ Power of Ligand $\longleftarrow \lambda$

$\longrightarrow \Delta_o$

So, for the given complexes, it is evidented from the plot (Absorption vs. λ)

$$\underset{(C)}{\lambda^{(ii)}_{max}} > \underset{(B)}{\lambda^{(i)}_{max}} > \underset{(A)}{\lambda^{(iii)}_{max}}$$
$$[F^-] \quad [NCS^-] \quad [NH_3]$$

89 For octahedral Mn (II) and tetrahedral Ni (II) complexes, consider the following statements :

(I) Both the complexes can be high spin.

(II) Ni(II) complex can very rarely be low spin.

(III) With strong field ligands, Mn(II) complexes can be low spin.

(IV) Aqueous solution of Mn(II) ions is yellow in colour.

The correct statements is

(a) (I) and (II) only **[2020, 2 Sep Shift-I]**

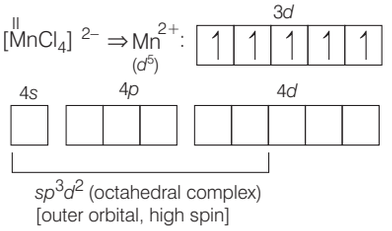
(b) (II), (III) and (IV) only

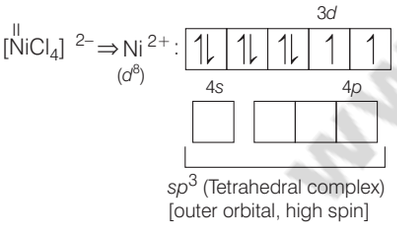
(c) (I), (II) and (III) only

(d) (I), (III) and (IV) only

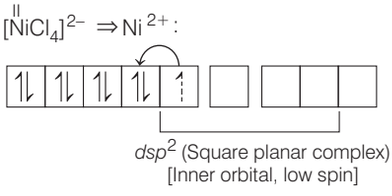
Ans. ***(c)***

I. In presence of weak field ligand like Cl^-, both octahedral Mn(II) and tetrahedral Ni(II) complexes can be high spin, like

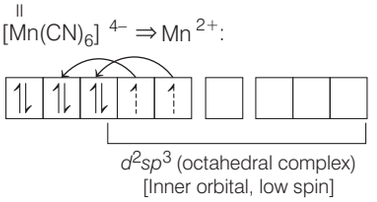




II. In presence of strong field ligand like CN^-, Ni^{2+} can form low spin square planar complex.



III. With strong field ligands like $-CN^-$, Mn(II) octahedral complexes can be low spin,



IV. Aqueous solution of Mn(II) ion is pale pink in colour.

Hence, statement I, II and III are correct whereas statement IV is incorrect.

90 Consider that a d^6 metal ion (M^{2+}) forms a complex with *aqua* ligands and the spin only magnetic moment of the complex is 4.90 BM. The geometry and the crystal field stabilisation energy of the complex is **[2020, 2 Sep Shift-I]**

(a) tetrahedral and $-1.6\Delta_t + 1P$

(b) octahedral and $-2.4\ \Delta_0 + 2P$

(c) octahedral and $-1.6\ \Delta_0$

(d) tetrahedral and $-0.6\ \Delta_t$

Ans. ***(d)***

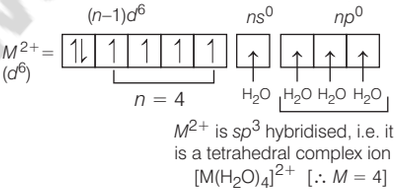
$$\underset{(d^6)}{M^{2+}} + mH_2O \longrightarrow [M(H_2O)_m]^{2+}$$

Here, H_2O is a weak field ligand and it should give a high spin paramagnetic ($\mu = 4.90$ BM) complex ion.

We know, $\mu = \sqrt{n(n+2)}$ BM

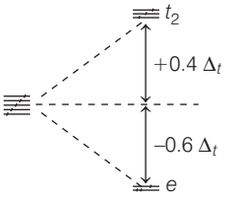
$= 4.90$ BM $(n = 4)$

[$\because n$ = Number of unpaired electrons in the complex]

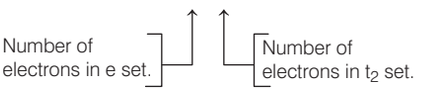


M^{2+} is sp^3 hybridised, i.e. it is a tetrahedral complex ion $[M(H_2O)_4]^{2+}$ [$\because M = 4$]

So, the complex will experience splitting of $(n-1)d$-orbitals in tetrahedral field.



$CFSE = [(-0.6) \times 3 + (0.4) \times 3]\Delta_t = -0.6\ \Delta_t$



So, the geometry and the crystal field stabilisation energy of the complex is tetrahedral and $-0.6\Delta_t$ respectively.

91 The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ shows a single broad peak with a maximum at 20,300 cm^{-1}. The crystal field stabilisation energy (CFSE) of the complex ion, in kJ mol^{-1}, is (1 kJ $mol^{-1} = 83.7$ cm^{-1}) **[2020, 3 Sep Shift-I]**

(a) 145.5 (b) 242.5

(c) 83.7 (d) 97

Ans. ***(d)***

In $[Ti(H_2O)]^{3+}$, Ti^{3+} ion of d^1 configuration is present in the octahedral complex. Under octahedral crystal field, the configuration of Ti^{3+} will be, $t^1_{2g}e^0_g$.

So, $CFSE = [(-0.4) \times 1 + (+0.6) \times 0]\ \Delta_0$

$= -0.4 \times \Delta_0 = -0.4 \times 20{,}300$ cm^{-1}

[$\because \Delta_0 = 20{,}300$ cm^{-1}]

$= -0.4 \times \dfrac{20{,}300}{83.7}$ kJ mol^{-1}

[$\because 1$ kJ $mol^{-1} = 83.7$ cm^{-1}]

$= -97.103$ kJ mol^{-1}

$\Rightarrow$ CFSE $= 97$ kJ mol^{-1}

92 The *d*-electron configuration of $[Ru(en)_3]Cl_2$ and $[Fe(H_2O)_6]Cl_2$, respectively are **[2020, 3 Sep Shift-II]**

(a) $t^6_{2g}\ e^0_g$ and $t^6_{2g}e^0_g$

(b) $t^6_{2g}\ e^0_g$ and $t^4_{2g}e^2_g$

(c) $t^4_{2g}\ e^2_g$ and $t^6_{2g}e^0_g$

(d) $t^4_{2g}\ e^2_g$ and $t^4_{2g}e^2_g$

Ans. ***(b)***

The *d*-electron configuration $[Ru(en)_3]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ respectively are $t^6_{2g}e^0_g$ and $t^4_{2g}e^2_g$.

$[Ru(en)_3]Cl_2$

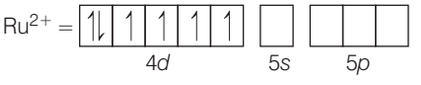
Ru = 4*d* series

en = bidentate ligand (strong field ligand)

C.N. = 6

Oxidation number + 2

$Ru^{2+} = [Kr]\,4d^6\,5s^0$



In presence of en, pairing should be done

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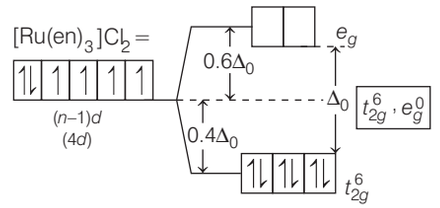
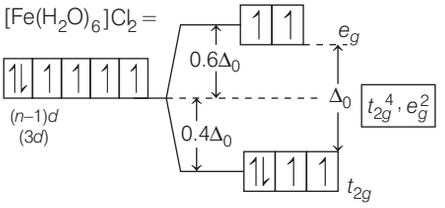


For $[Fe(H_2O)_6]Cl_2$ $\Rightarrow H_2O$ (weak field ligand)

Oxidation number $= +2$; C.N. $= 6$

$Fe^{2+} = 3d^6$



93 The pair in which both the species have the same magnetic moment (spin only) is **[2020, 4 Sep Shift-I]**

(a) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)]^{2+}$

(b) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$

(c) $[Co(OH)_4]^{2-}$ and $[Fe(NH_3)_6]^{2+}$

(d) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

Ans. ***(b)***

The pairs in which both the species have same magnetic moment is $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$.

All the given options is described as follows :

$[Mn(H_2O)_6]^{2+}$

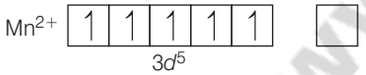
Electronic configuration,

$Mn = 3d^5 4s^2$ or $Mn^{2+} = 3d^5$

Here, coordination number = 6

Oxidation number = +2

Weak field ligand = H_2O



Hence, unpaired electrons are 5.

$[Cr(H_2O)_6]^{2+}$

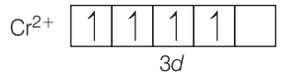
Electronic configuration, $Cr = 2d^5 4s^1$

or $Cr^{2+} = 3d^4$

Here, coordination number = 6

Oxidation number = +2

Weak field ligand = H_2O



Hence, unpaired electrons are 4.

$[Fe(H_2O)_6]^{2+}$

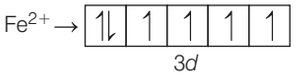
Electronic configuration, $Fe = 3d^6 4s^2$

or $Fe^{2+} = 3d^6$

Here, coordination number = 6

Oxidation number = +2

Weak field ligand = H_2O



Hence, unpaired electrons are 4.

$[Co(OH)_4]^{2-}$

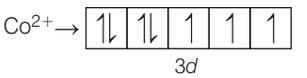
Electronic configuration, $Co = 3d^7 4s^2$

or $Co^{2+} = 3d^7$

Here, coordination number = 4

Oxidation number = +2

Weak field ligand = OH



Hence, unpaired electrons are 3.

$[Fe(NH)_3]_6$

Electronic configuration, $Fe = 3d^6 4s^2$

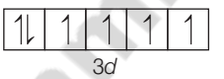
or $Fe^{2+} = 3d^6$

Here, coordination number = 6

Oxidation number = 2

Weak field ligand = NH_3

NH_3 is SFL (strong field ligand) but act as a weak field ligand with Fe^{2+}.



Hence, unpaired electrons are 4.

$[CoCl_4]^{2-}$

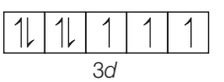
Electronic configuration, $Co = 3d^7 4s^2$

or $Co^{2+} = 3d^7$

Here, coordination number = 4

Oxidation number = +2

Weak field ligand = Cl



Hence, unpaired electrons = 3

94 The one that can exhibit highest paramagnetic behaviour among the following is **[2020, 4 Sep Shift-II]**

gly = glycinato;

bpy = 2, 2′-bipyridine

(a) $[Pd(gly)_2]$

(b) $[Fe(en)(bpy)(NH_3)_2]^{2+}$

(c) $[Co(OX)_2(OH)_2]^{-}(\Delta_0 > P)$

(d) $[Ti(NH_3)_6]^{3+}$

Ans. ***(d)***

	Complex	Electronic configuration	Number of unpaired electron	Magnetic behaviour
(a)	$[Pd(gly)_2]$	$Pd^{2+} = 4d^8$	0	Diamagnetic
(b)	$[Fe(en)(bipy)(NH_3)_2]^{2+}$	$Fe^{2+} = 3d^6 \rightarrow t_{2g}^6, e_g^0$	0	Diamagnetic
(c)	$[Co(ox)_2(NH_3)_2]^{-}$ $(\Delta_0 > P)$	$Co^{3+} = 3d^6 \rightarrow t_{2g}^6, e_g^0$	0	Diamagnetic
(d)	$[Ti(NH_3)_6]^{3+}$	$Ti^{3+} = 3d^1 \rightarrow t_{2g}^1, e_g^0$	1	Paramagnetic

The paramagnetism of a complex is expressed in terms of magnetic moment (μ). Greater is the number of unpaired electrons in the central atom/ion of given compound, greater is its paramagnetic character among the given option $[Ti(NH_3)_6]^{3+}$ have unpaired electron so, it exhibit highest paramagnetic behaviour.

95 The molecule in which hybrid MOs involve only one *d*-orbital of the central atom is **[2020, 4 Sep Shift-II]**

(a) XeF_4 (b) $[CrF_6]^{3-}$

(c) BrF_5 (d) $[Ni(CN)_4]^{2-}$

Ans. ***(d)***

	Molecule	Hybridisation
(a)	XeF_4	sp^3d^2
(b)	$[CrF_6]^{3-}$	d^2sp^3
(c)	BrF_5	sp^3d^2
(d)	$[Ni(CN)_4]^{2-}$	dsp^2

In $[Ni(CN)_4]^{2-}$ molecule hybrid MOs involve only one *d*-orbital of the central atom.

96 The crystal field stabilisation energy (CFSE) of $[CoF_3(H_2O)_3]$ $(\Delta_0 < P)$ is **[2020, 4 Sep Shift-II]**

(a) $-0.8\,\Delta_0$ (b) $-0.8\Delta_0 + 2P$

(c) $-0.4\Delta_0$ (d) $-0.4\Delta_0 + P$

Ans. ***(c)***

$[CoF_3(H_2O)_3]$ is an octahedral complex.

In this complex (compound) all ligands are weak field ligand.

With weak field ligands $\Delta_0 < P$ (pairing energy), so the electronic configuration of Co (III) will be $t_{2g}^4 e_g^2$, i.e. it has four unpaired electrons.

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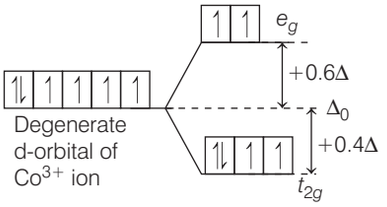


Here, CFSE can be calculated as :

$CFSE = [-04.x + 0.6y]\,\Delta_0$

Where, Δ_0 = CFSE in octahedral complex

x = Number of electrons in t_{2g} orbitals

y = Number of unpaired electrons in e_g orbitals

$= [-0.4 \times 4 + 0.6 \times 2]\,\Delta_0 + 0$

$= [-1.6 + 1.2]\,\Delta_0 = [-0.4\,\Delta_0]$

Hence, the crystal field stabilisation energy (CFSE) of $[CoF_3(H_2O)_3]$ will be $-0.4\,\Delta_0$.

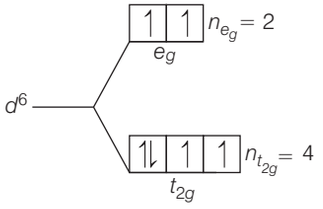
97 The values of the crystal field stabilisation energies for a high spin d^6 metal ion in octahedral and tetrahedral fields respectively, are **[2020, 5 Sep Shift-I]**

(a) $-0.4\,\Delta_0$ and $-0.27\,\Delta_t$
(b) $-1.6\,\Delta_0$ and $-0.4\,\Delta_t$
(c) $-2.4\,\Delta_0$ and $-0.6\,\Delta_t$
(d) $-0.4\,\Delta_0$ and $-0.6\,\Delta_t$

Ans. ***(d)***

Crystal field stabilisation energy (CFSE) for high spin d^6 metal ion.

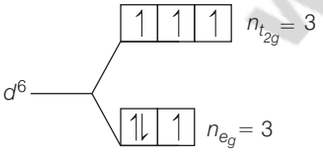
Crystal field splitting in octahedral field.



$CFSE = [-0.4 n_{t_{2g}} + 0.6 n_{e_g}]\,\Delta_0$

$= [-0.4 \times 4 + 0.6 \times 2]\,\Delta_0 = -0.4\,\Delta_0$

Crystal field splitting in tetrahedral field



$CFSE = (-0.6\, n_{e_g} + 0.4 n_{t_{2g}})\,\Delta_t$

$= (-0.6 \times 3 + 0.4 \times 3)\,\Delta_t$

$= (-1.8 + 1.2)\Delta_t = -0.6\,\Delta_t$

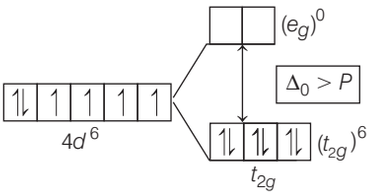
98 Considering that $\Delta_0 > P$, the magnetic moment (in BM) of $[Ru(H_2O)_6]^{2+}$ would be ..... . **[2020, 5 Sep Shift-II]**

Ans. ***(0)***

Magnetic moment (in BM) of $[Ru(H_2O)_6]^2$ would be; while considering that $\Delta_0 > P$,

$Ru_{(44)}$:$[Kr]4d^7\,5s^1$ (in ground state)

$\Rightarrow$ In $Ru^{2+} \Rightarrow 4d^6 \Rightarrow (t_2g)^6(e_g)^0$



$\Rightarrow$ Here, number of unpaired electrons in

$Ru^{2+} = (t_{2g})^6(e_g)^0 = 0$ and hence

$\mu = \sqrt{n(n+2)}\,BM = 0\,BM$

99 The species that has a spin-only magnetic moment of 5.9 BM, is (T_d = tetrahedral) **[2020, 6 Sep Shift-I]**

(a) $[Ni(CN)_4]^{2-}$ (square planar)
(b) $[NiCl_4]^{2-}(T_d)$
(c) $[Ni(CO)_4](T_d)$
(d) $[MnBr_4]^{2-}(T_d)$

Ans. ***(d)***

Given that $\sqrt{n(n+2)} = 5.91$ BM.

$\therefore \quad n = 5$

	Complex	Electronic configuration	Unpaired electron	Ligand
(b)	$[NiCl_4]^{2-}$	$Ni^{2+} = [Ar]3d^8$	2	(Cl^-) Weak
(a)	$[Ni(CN)_4]^{2-}$	$Ni^{2+} = [Ar]3d^8$	0	$(CN)^-$ Strong
(c)	$[Ni(CO)_4]$	$Ni = [Ar]3d^8$	2	(CO) Strong
(d)	$[MnBr_4]^{2-}$	$Mn^{2+} = [Ar]3d^5$	5	(Br^-) Weak

Only $[MnBr_4]^{2-}$ have 5 unpaired electrons, it is high spin complex due to weak ligand.

$\therefore$ Magnetic moment (γ) = $\sqrt{n(n+2)}$ BM $\Rightarrow n = 5$

$\therefore \quad (\gamma) = \sqrt{5(5+2)} = \sqrt{35}$, $\gamma = 5.9$ BM

Hence, the correct option is (d).

100 For a d^4 metal ion in an octahedral field, the correct electronic configuration is **[2020, 6 Sep Shift-II]**

(a) $t_{2g}^3 e_g^1$ when $\Delta_0 < P$
(b) $t_{2g}^3 e_g^1$ when $\Delta_0 > P$
(c) $t_{2g}^4 e_g^0$ when $\Delta_0 < P$
(d) $t_g^2 e_{2g}^2$ when $\Delta_0 < P$

Ans. ***(a)***

In octahedral complexes:

(i) If $\Delta_0 < P$ (weak field, high spin situation).
The fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.

(ii) If $\Delta_0 > P$ (strong field, low spin situation), pairing will occur in the t_{2g} level with e_g level remaining unoccupied giving configuration $t_{2g}^4 e_g^0$.

Hence, for d^4 metal ion in an octahedral field, the correct, electronic configuration is $t_{2g}^3 e_g^1$, when $\Delta_0 < P$.

101 Among the statements (*A*)-(*D*), the incorrect ones are

(*A*) octahedral Co(III) complexes with strong, field ligands have very high magnetic moments
(*B*) When $\Delta_0 < P$, the *d*-electron configuration of Co(III) in an octahedral complex is t_{eg}^4, e_g^2
(*C*) Wavelength of light absorbed by $[Co(en)_3]^{3+}$ is lower than that of $[CoF_6]^{3-}$
(*D*) If the Δ_0 for an octahedral complex of Co(III) is 18,000 cm^{-1}, the Δ_t for its tetrahedral complex with the same ligand will be 16,000 cm^{-1} **[2020, 7 Jan Shift-II]**

(a) *B* and *C* only (b) *A* and *B* only
(c) *C* and *D* only (d) *A* and *D* only

Ans. ***(d)***

(A) Co^{3+} has d^6 configuration with strong field ligands, the configuration becomes $t_{2g}^6 e_g^0$.
As no unpaired electron is present in Co^{3+}, so it has zero magnetic moment.
$\therefore$ Statement is incorrect.

(B) When $\Delta_o < P$, pairing of *d*-electrons takes place only after filling every orbital with single electron.
$\therefore$ Configuration of $d^6 = t_{2g}^4\, e_g^2$
Statement is correct.

(C) 'en' or ethan-1, 2-diamine has greater field strength than F^-.
$\therefore$ Frequency of light absorbed in $[Co(en)_3]^{3+}$ is greater and wavelength is lower than $[CoF_6]^{3-}$.
Thus, this statement is correct.

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(D) $\Delta_t \approx \frac{4}{9}\Delta_o$ for complexes with same metal and ligand.

$\therefore \Delta_t$ must be $\frac{4}{9} \times 18000$

$= 8000 cm^{-1}$.

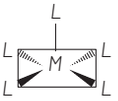
This statement is incorrect.

Hence, among the given options, option (d) is correct.

102 Complexes (ML_5) of metals Ni and Fe have ideal square pyramidal and trigonal bipyramidal geometries, respectively. The sum of the 90°, 120° and 180° *L-M-L* angles in the two complexes is ..... . **[2020, 8 Jan Shift-II]**

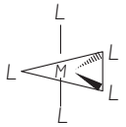
Ans. ***(20)***

Nickel : ML_5 complex is square pyramidal,



180° angles = 2
90° angles = 8
(4 in square plane
4 = perpendicular to plane)

Fe : ML_5 complex is trigonal bipyramidal



180° angle =1
90° angle = 6
120° angle = 3

Sum of all *L-M-L* angles in two complexes is = 2 + 8 + 1 + 6 + 3 = 20

103 The correct order of the calculated spin only magnetic moments of complexes (A) to (D) is **[2020, 8 Jan Shift-II]**

(A) $Ni(CO)_4$

(B) $[Ni(H_2O)_6]Cl_2$

(C) $Na_2[Ni(CN)_4]$

(D) $PdCl_2(PPh_3)_2$

(a) (A) ≈ (C) < (B) ≈ (D)

(b) (C) ≈ (D) < (B) < (A)

(c) (C) < (D) < (B) < (A)

(d) (A) ≈ (C) ≈ (D) < (B)

Ans. ***(d)***

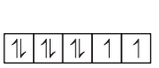
(A) : $Ni(CO)_4$

Ni has $3d^8 4s^2$ configuration and tetrahedral (strong field ligand).

$\therefore$ Unpaired electrons = 0, $\mu = 0$ BM

(B) : $[Ni(H_2O)_6]Cl_2$

Ni^{2+} has (d^8) configuration and has unpaired electrons.

$[Ni(H_2O)_6]^{2+} =$ 

$\mu = \sqrt{n(n+2)} = \sqrt{2\times4} = \sqrt{8}$ B.M = 2.82 BM

(C) : $Na_2[Ni(CN)_4]$

Ni^{2+} has (d^8) configuration and square planar (strong field ligand).

$\therefore$ dsp^2 hybridisation and no unpaired electron

$\therefore$ $\mu = 0$ BM

(D) : $PdCl_2(PPh_3)_2$

Pd^{2+} has (d^8) configuration. All coordination number = 4

Complexes of Pd^{2+} are square planar.

$\therefore$ dsp^2 hybridised.

No unpaired electron, $\mu = 0$ BM

The correct order of the calculated spin only magnetic moments of complexes is

$\mu(B) > \mu(A) = \mu(C) = \mu(D)$.

104 $[Pd(F)(Cl)(Br)(I)]^{2-}$ has *n* number of geometrical isomers. Then, the spin-only magnetic moment and crystal field stabilisation energy [CFSE] of $[Fe(CN)_6]^{n-6}$ respectively, are **[2020, 9 Jan Shift-II]**

[**Note** Ignore the pairing energy]

(a) 1.73 BM and $-2.0\Delta_o$

(b) 2.84 BM and $-1.6\Delta_o$

(c) 0 BM and $-2.4\Delta_o$

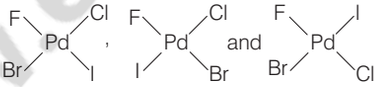
(d) 5.92 BM and 0

Ans. ***(a)***

Pd^{2+} complexes with coordination number = 4 are of square planar geometry, irrespective of the field strength of ligands.

For square planar complex with four different ligands, three, geometrical isomers are possible.

These are as follows :

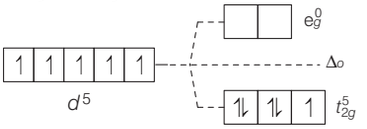


$\therefore$ $n = 3$

$[Fe(CN)_6]^{n-6} = [Fe(CN)_6]^{-3}$. So, oxidation state of iron in $[Fe(CN)_6]^{-3}$ is +3.

$Fe^{3+} = d^5$.

It forms a low spin complex (CN^- is a strong field ligand).



$\therefore$ Number of unpaired electrons (n) = 1

Spin only magnetic moment = $\sqrt{3}$ = 1.73 BM

$\mu_s = \sqrt{n(n+2)}$ BM

CFSE = (Number of electrons in $t_{2g} \times -0.4\Delta_o$) + (Number of electrons in $e_g \times 0.6\Delta_o$). = $5 \times -0.4\Delta_o = -2.0\Delta_o$.

105 The correct order of the spin only magnetic moments of the following complexes is **[2020, 9 Jan Shift-II]**

(I) $[Cr(H_2O)_6]Br_2$

(II) $Na_4[Fe(CN)_6]$

(III) $Na_3[Fe(C_2O_4)_3]$ ($\Delta_0 > P$)

(IV) $(Et_4N)_2[CoCl_4]$

(a) (II) ≈ (I) > (IV) > (III)

(b) (I) > (IV) > (III) > (II)

(c) (III) > (I) > (IV) > (II)

(d) (III) > (I) > (II) > (IV)

Ans. ***(d)***

I. In $[Cr(H_2O)_6]Br_2$, chromium is in Cr^{2+} having electronic configuration $[Ar]3d^4$.

H_2O is a weak field ligand.

It has octahedral geometry

$\therefore$ $3d^4 = t_{2g}^3 e_g^1$

Unpaired electrons = 4

$\mu_s = \sqrt{4\times6} = \sqrt{24}$ BM.

II. $Na_4[Fe(CN)_6] \longrightarrow Fe^{2+} = [Ar]3d^6$

CN^- is a strong field ligand

Octahedral geometry

$\therefore$ $3d^6 = t_{2g}^6 e^0 g$

Unpaired electrons = 0

$\mu_s = 0$

III. $Na_3[Fe(C_2O_4)_3] \longrightarrow Fe^{3+} = [Ar]3d^5$

$\Delta_o > p$(Given)

Octahedral geometry

$\therefore$ $3d^5 = t_{2g}^5 e_g^0$

Unpaired electrons = 1;

$\mu_s = \sqrt{3} = 1.73$ BM

IV. $(Et_4N)_2[CoCl_4][CoCl_4]^{2-}$:

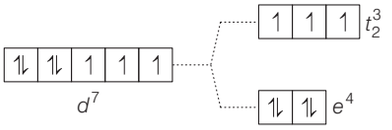
$Co^{2+} = [Ar]3d^7$

Cl^- is a weak field ligand.

In this complex, coordination number is 4

Tetrahedral geometry

Splitting of *d* - orbitals in tetrahedral field is



Unpaired electrons = 3

$\mu_s = \sqrt{15}$ BM

$\therefore$ Spin only magnetic moment order is :

I > IV > III > II

106 The correct order of the spin only magnetic moment of metal ions in the following low spin complexes, $[V(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$, $[Ru(NH_3)_6]^{3+}$, and $[Cr(NH_3)_6]^{2+}$, is **[2019, 8 April Shift-I]**

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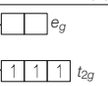
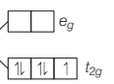
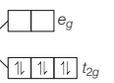
(a) $Cr^{2+} > Ru^{3+} > Fe^{2+} > V^{2+}$
(b) $V^{2+} > Cr^{2+} > Ru^{3+} > Fe^{2+}$
(c) $V^{2+} > Ru^{3+} > Cr^{2+} > Fe^{2+}$
(d) $Cr^{2+} > V^{2+} > Ru^{3+} > Fe^{2+}$

Ans. ***(b)***

Key Idea In presence of strong field ligands, $\Delta_o > P$, for fourth electron it is more energetically favourable to occupy t_{2g} orbital with configuration $t_{2g}^4 e_g^0$ and form low spin complexes.

The correct order of the spin only magnetic moment of metal ions in the given low-spin complexes is $V^{2+} > Cr^{2+} > Ru^{3+} > Fe^{2+}$.

All the given complexes possess strong field ligands (CN, NH_3). Hence, readily form low spin complexes.

Complex	Oxidation state	Configuration	Orbital splitting	No. of unpaired electrons
$[V(CN)_6]^{4-}$	V^{2+}	$t_{2g}^3 e_g^0$		3
$[Cr(NH_3)_6]^{2+}$	Cr^{2+}	$t_{2g}^4 e_g^0$		2
$[Ru(NH_3)_6]^{3+}$	Ru^{3+}	$t_{2g}^5 e_g^0$		1
$[Fe(CN)_6]^{4-}$	Fe^{2+}	$t_{2g}^6 e_g^0$		0

107 The crystal field stabilisation energy (CFSE) of $[Fe(H_2O)_6]Cl_2$ and $K_2[NiCl_4]$, respectively, are **[2019, 10 April Shift-II]**

(a) $-0.4\,\Delta_o$ and $-1.2\,\Delta_t$
(b) $-0.4\,\Delta_o$ and $-0.8\,\Delta_t$
(c) $-2.4\,\Delta_o$ and $-1.2\,\Delta_t$
(d) $-0.6\,\Delta_o$ and $-0.8\,\Delta_t$

Ans. ***(b)***

Key Idea Crystal field stabilisation energy (CFSE) for octahedral complexes

$= (-0.4x + 0.6y)\Delta_o$

where, x = number of electrons occupying t_{2g} orbital.

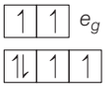
y = number of electrons occupying e_g orbital.

CFSE for tetrahedral complexes $= (-0.6x + 0.4y)\Delta_t$

where, x = number of electrons occupying e orbital.

y = number of electrons occupying t orbital.

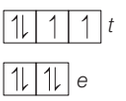
In $[Fe(H_2O)_6]Cl_2$, H_2O is a weak field ligand, so it is a high spin (outer orbital) octahedral complex of Fe^{2+}.

$Fe^{2+}(3d^6) =$  (e_g above, t_{2g} below)

$\therefore$ CFSE $= (-0.4x + 0.6y)\Delta_o$

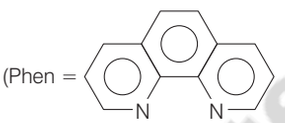
$= [-0.4 \times 4 + 0.6 \times 2]\Delta_o = -0.4\Delta_o$

In $K_2[NiCl_4]$, Cl^- is a weak field ligand, so it is a high spin tetrahedral complex of Ni^{2+}.

$Ni^{2+}(3d^6) =$  (t above, e below)

$\therefore$ CFSE $= (-0.6 \times 4 + 0.4 \times 4)\Delta_t = -0.8\Delta_t$

108 The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to +3 state is **[2019, 12 April Shift-I]**



Ignore pairing energy

(a) $[Co(phen)_3]^{2+}$
(b) $[Ni(phen)_3]^{2+}$
(c) $[Zn(phen)_3]^{2+}$
(d) $[Fe(phen)_3]^{2+}$

Ans. ***(d)***

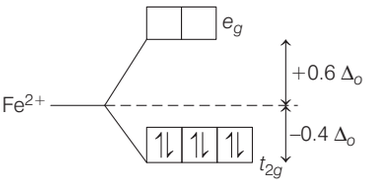
Key Idea Crystal field splitting occurs due to the presence of ligands in a definite geometry. In octahedral complexes the energy of two, e_g orbitals will increase by $(0.6)\Delta_o$ and that of three t_{2g} will decrease by $(0.4)\Delta_o$.

The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to +3 state is $[Fe(phen)_3]^{2+}$.

$[Fe(phen)_3]^{2+} \xrightarrow{-e^-} [Fe(phen)_3]^{3+}$

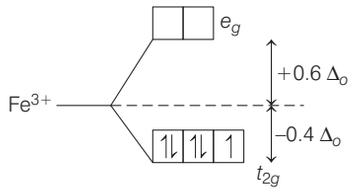
In $[Fe(phen)_3]^{2+}$, electronic configuration of Fe^{2+} is $3d^6 4s^0$.

Phenanthrene is a strong field symmetrical bidentate ligand. The splitting of orbital in Fe^{2+} is as follows:



CFSE $= 6 \times -0.4\Delta_o = -2.4\Delta_o$.

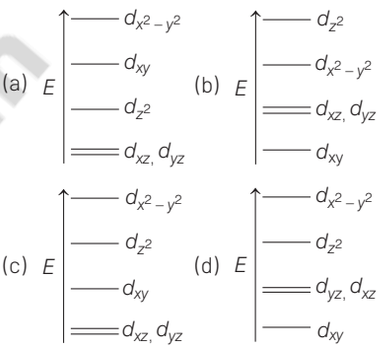
The splitting of orbital and arrangement of electrons in Fe^{3+} is as follows :



CFSE $= 5 \times -0.4\,\Delta_o = -2.0\,\Delta_o$

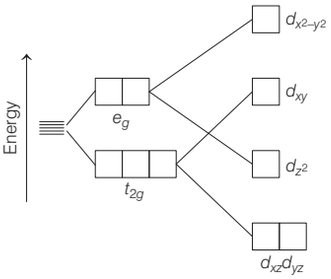
Fe^{2+} upon oxidation of its metal to +3 state lose its CFSE from $-2.4\,\Delta_o$ to $-2.0\Delta_o$.

109 Complete removal of both the axial ligands (along the z-axis) from an octahedral complex leads to which of the following splitting patterns? (relative orbital energies not on scale). **[2019, 12 April Shift-I]**



Ans. ***(a)***

Complete removal of both the axial ligands (along the z-axis) from an octahedral complex leads to the following splitting pattern.



The single electron in the $d_{x^2-y^2}$ orbital is being repelled by four ligands, while the electron in the d_{z^2} orbital is only being repelled

by two ligands. Thus, the energy of the $d_{x^2-y^2}$ increases relative to that of d_{z^2}.

A more stable arrangement arises when both the e_g electrons pair up and occupy the lower energy d_{z^2} orbital. This leaves the $d_{x^2-y^2}$ orbital empty.

Thus, four ligands can now approach along $+x, -x, +y$ and $-y$ directions without any difficulty as $d_{x^2-y^2}$ orbital is

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empty. However, ligands approaching along $+z$ and $-z$ directions meet very strong repulsive forces from filled d_{z^2} orbitals. Thus, only four ligands succeed in bonding to the metal. A square planar complex is formed, the attempt to form an octahedral complex being unsuccessful.

110 Two complexes $[Cr(H_2O)_6]Cl_3$ (*A*) and $[Cr(NH_3)_6]Cl_3$ (*B*) are violet and yellow coloured, respectively. The incorrect statement regarding them is

(a) Δ_o value for (*A*) is less than that of (*B*)
(b) both absorb energies corresponding to their complementary colours
(c) Δ_o values of (*A*) and (*B*) are calculated from the energies of violet and yellow light, respectively
(d) both are paramagnetic with three unpaired electrons

[2019, 9 Jan Shift-I]

Ans. ***(c)***

'*A*' absorbs yellow light of less energy and emits violet light of high energy (complementary colour) because H_2O is a weak field ligand. But in case of '*B*', due to presence of strong field ligand (NH_3), it absorbs high energy violet light and emits low energy complementary yellow colour.

Δ(CFSE) is measured with help of wavelength of the colour absorbed by the given coordination compound, as

$$\Delta_o = h\nu = h \times \frac{c}{\lambda}$$

Both the complexes contain three unpaired electrons. Therefore, both are paramagnetic.

111 The complex that has highest crystal field splitting energy (Δ), is

[2019, 9 Jan Shift-II]

(a) $[Co(NH_3)_5Cl]Cl_2$
(b) $[Co(NH_3)_5(H_2O)]Cl_3$
(c) $K_3[Co(CN)_6]$
(d) $K_2[CoCl_4]$

Ans. ***(c)***

All of the complex given are the octahedral complexes of Co (III) except $K_2[CoCl_4]$, which is a tetrahedral complex of Co (II) (sp^3-hybridised).

We know, $\Delta_t < \Delta_O \quad \left[\because \Delta_t = \frac{4}{9}\Delta_O\right]$

So, the octahedral complexes (*a*, *b*, *c*) have higher Δ_o values than that of tetrahedral, $K_2[CoCl_4]$.

Now, for the complexes, *a*, *b* and *c*, the magnitude of $\Delta_O \propto$ ligand strength, which is based on their positions in the spectrochemical series.

$$Cl^- < H_2O < NH_3 < CN^-$$

Hence, $K_3[Co(CN)_6]$ will have the highest Δ value.

112 Homoleptic octahedral complexes of a metal ion 'M^{3+}' with three monodentate ligands L_1, L_2 and L_3 absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligand strength is **[2019, 9 Jan Shift-II]**

(a) $L_1 < L_2 < L_3$ (b) $L_2 < L_1 < L_3$
(c) $L_3 < L_1 < L_2$ (d) $L_3 < L_2 < L_1$

Ans. ***(c)***

In homoleptic complexes, the metal atom/ion is linked to only one type of ligand. Assuming, ligands are neutral, the octahedral complexes of M^{3+} can be,

$$\underset{(I)}{[M(L_1)_6]^{3+}}, \underset{(II)}{[M(L_2)_6]^{3+}} \text{ and } \underset{(III)}{[M(L_3)_6]^{3+}}$$

$\lambda_{Absorption}$ Green Blue Red (wavelength)

So, $\lambda_{III}^{L_3} > \lambda_{I}^{L_1} > \lambda_{II}^{L_2}$

$\therefore \Delta^{\circ}_{absorption}$: $\Delta_{II}^{L_2} > \Delta_{I}^{L_1} > \Delta_{III}^{L_3}$

$$[\because \text{Energy}(\Delta, \text{CFSE}) \propto \frac{1}{l}]$$

We know, ligand strength $\propto \Delta^{\circ}_{absorption}$

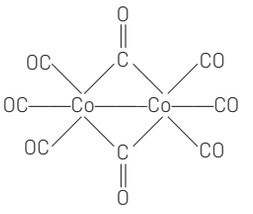
So, the increasing order of the ligand strength will be, $L_3 < L_1 < L_2$

113 The number of bridging CO ligand(s) and Co—Co bond(s) in $Co_2(CO)_8$, respectively are **[2019, 11 Jan Shift-II]**

(a) 2 and 0 (b) 0 and 2
(c) 4 and 0 (d) 2 and 1

Ans. ***(d)***

The structure of $Co_2(CO)_8$ (a polynuclear metal carbonyl) can be written as :



Total number of bridging CO ligands = 2 and the Co—Co bond = 1

114 $Mn_2(CO)_{10}$ is an organometallic compound due to the presence of

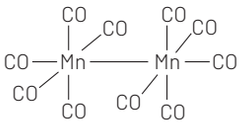
(a) Mn—C bond (b) Mn—O bond
(c) C—O bond (d) Mn—Mn

[2019, 12 Jan Shift-I]

Ans. ***(a)***

$Mn_2(CO)_{10}$ is an organometallic compound due to the presence of Mn—C bond. The metal-carbon bond in organometallic compounds possess both σ and π-character. The *M*—C σ-bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The *M*—C π-bond is formed by the donation of pair of electrons from a filled *d*-orbital of metal into vacant antibonding π^* orbital of CO. The *M*—*L* bonding creates a synergic effect which strengthens the bond between CO and the metal.

The structure of $Mn_2(CO)_{10}$ is shown below :



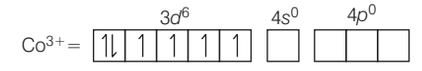
115 The metal *d*-orbitals that are directly facing the ligands in $K_3[Co(CN)_6]$ are

(a) d_{xz}, d_{yz} and d_{z^2} (b) $d_{x^2-y^2}$ and d_{z^2}
(c) d_{xy}, d_{xz} and d_{yz} (d) d_{xz} and $d_{x^2-y^2}$

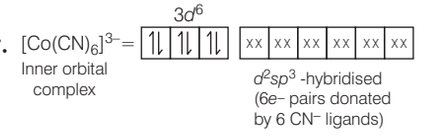
[2019, 12 Jan Shift-I]

Ans. ***(b)***

In $K_3[Co(CN)_6]$, Co have +3 oxidation state and electronic configuration of Co^{3+} is $[Ar]_{18}\, 3d^6$.



As, CN^- is a strong field ligands so it pairs up the de^-s



In an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners. The lobes of the *eg* orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes *x*, *y* and *z* under the influence of an octahedral field, the *d*-orbitals split as follow.

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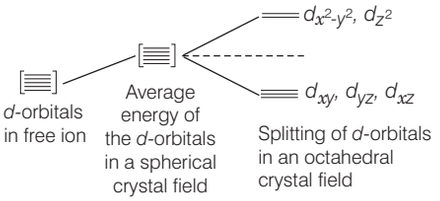


As the *d*-orbitals, i.e. $d_{x^2-y^2}$ and d_{z^2} are vacant.

Hence, these both orbitals are directly facing the ligands in $K_3[Co(CN)_6]$.

116 The magnetic moment of an octahedral homoleptic Mn(II) complex is 5.9 BM. The suitable ligand for this complex is

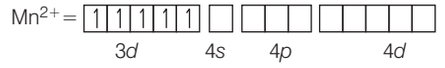
(a) CN^-
(b) ethylenediamine
(c) NCS^-
(d) CO **[2019, 12 Jan Shift-II]**

Ans. ***(c)***

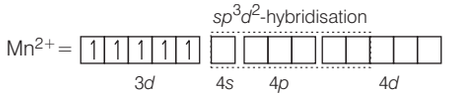
The magnetic moment of the magnitude 5.9 BM suggest the presence of 5 unpaired electrons in Mn(II). This can be cross verified by putting the value (5) of unpaired electrons in the formula,

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

Thus, the valence electronic configuration of Mn(II) in the complex is



The octahedral homoleptic complex suggests sp^3d^2-hybridisation in the complex, i.e.



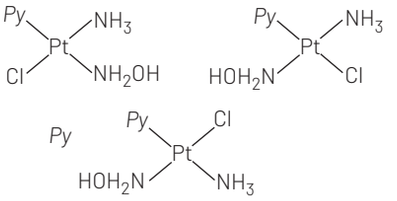
Thus, 5 unpaired electrons are present in the complex which suggest the presence of a weak ligand like NCS.

117 The number of geometric isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is (py = pyridine) **[JEE Main 2015]**

(a) 2 (b) 3
(c) 4 (d) 6

Ans. ***(b)***

$[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is square planar complex. The structures are formed by fixing a group and then arranging all the groups.



Hence, this complex shows three geometrical isomers.

118 Which of the following compounds is not coloured yellow?

(a) $Zn_2[Fe(CN)_6]$ **[JEE Main 2015]**
(b) $K_3[Co(NO_2)_6]$
(c) $(NH_4)_3[As(Mo_3O_{10})_4]$
(d) $BaCrO_4$

Ans. ***(a)***

$Zn_2[Fe(CN)_6]$, $K_3[Co(NO_2)_6]$ and $[(NH_4)_3As(Mo_3O_{10})_4]$ show colour due to *d-d* transition while $BaCrO_4$ is coloured due to charge transfer phenomenon.

Further, according to spectrochemical series the strong ligand possessing complex has higher energy and hence lower wavelength. Therefore, complexes containing NO_2, NH_4^+, O^{2-} etc ligands show yellow colour while CN^- forces the complex to impart white colour.

Spectrochemical Series

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN < py < NH_3 < en < bipy < Phen < NO_2^- < PPh_3 < CN^- \approx CO$$

119 The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is **[JEE Main 2014]**

(a) $L_4 < L_3 < L_2 < L_1$
(b) $L_1 < L_3 < L_2 < L_4$
(c) $L_3 < L_2 < L_4 < L_1$
(d) $L_1 < L_2 < L_4 < L_3$

Ans. ***(b)***

Ligand	L_1	L_2	L_3	L_4
Coloured region of absorbed wavelength	Red	Green	Yellow	Blue

Coloured regions of visible light (VIBGYOR) are arranged in the increasing order of wavelength or decreasing order of energy [$\because E \propto 1/\lambda$]. Therefore,

$$E_{\underset{(L_1)}{\text{Red}}} < E_{\underset{(L_2)}{\text{yellow}}} < E_{\underset{(L_3)}{\text{green}}} < E_{\underset{(L_4)}{\text{blue}}}$$

This suggests that L_4 will absorbs higher energy wavelength followed by L_2, L_3 and L_1. Since, higher absorbed energy corresponds to greater extent of crystal field splitting and thus, higher field strength of the ligand.

Hence, the increasing order of ligand strength of the four ligands is $L_1 < L_3 < L_2 < L_4$

120 Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong? **[AIEEE 2011]**

(a) The complex involves d^2sp^3 hybridization and is octahedral in shape
(b) The complex is paramagnetic
(c) The complex is an outer orbital complex
(d) The complex gives white precipitate with silver nitrate solution

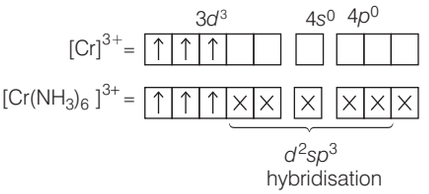
Ans. ***(c)***

$\underbrace{[Cr(NH_3)_6]}_{\text{Coordinate sphere}}$ $\underbrace{Cl_3}_{\text{Ionisable}}$ $\rightleftharpoons$

$[Cr(NH_3)_6]^{3+} + 3Cl^-$

$\xrightarrow{AgNO_3}$ $AgCl\downarrow$ White precipitate

In $[Cr(NH_3)_6]^{3+}$, Cr exists as Cr^{3+} ion. The outer orbital electronic configuration of Cr is $3d^3\,4s^0$. The orbital diagram is represented by



Here, $\boxed{\times}$ indicates lone-pair of NH_3 donated to Cr.

Hence,

(a) d^2sp^3-hybridization, octahedral. Thus, correct.
(b) There are three unpaired electrons, hence paramagnetic Thus, correct.
(c) d^2sp^3-inner orbital complex, thus incorrect.
(d) Due to ionizable Cl^- ions, white precipitate with $AgNO_3$, thus correct.

Therefore, (c) is wrong.

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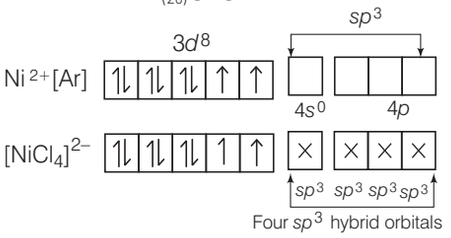
121 The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is **[AIEEE 2011]**

(a) 1.82 BM (b) 5.46 BM
(c) 2.82 BM (d) 1.41 BM

Ans. ***(c)***

$[NiCl_4]^{2-}$; oxidation number of Ni
, $x - 4 = -2$
$\therefore x = +2$, $Ni_{(28)}$ $[Ar]3d^8, 4s^2$



sp^3-hybrid orbitals, tetrahedral

Since, Cl^- is a weak ligand, thus unpaired electrons are not paired. Lone pairs from 4 Cl^- are accommodated in four sp^3 hybrid orbitats.

n = unpaired electron = 2, paramagnetic

Magnetic moment (spin only)
$= \sqrt{n(n+2)}$ BM $= \sqrt{8} = 2.828$ BM

122 In which of the following octahedral complexes of Co (At no. 27), will the magnitude of Δ_o be the highest? **[AIEEE 2008]**

(a) $[Co(CN)_6]^{3-}$
(b) $[Co(C_2O_4)_3]^{3-}$
(c) $[Co(H_2O)_6]^{3+}$
(d) $[Co(NH_3)_6]^{3+}$

Ans. ***(a)***

CFSE (crystal field splitting energy) for octahedral complex, Δ_o depends on the strength of negative ligand.
Spectrochemically, it has been found that the strength of splitting is as follows

$CO > \underline{CN^-} > NO_2^- > en > \underline{NH_3} > py >$
$NCS^- > H_2O > O^{2-} > OX^{2-} > OH^- > F^- >$
$Cl^- > SCN^- > S^{2-} > Br^- > I^-$

123 Which one of the following has a square planar geometry?
(At. no.
Co = 27, Ni = 28, Fe = 26, Pt = 78)
[AIEEE 2007]

(a) $[CoCl_4]^{2-}$ (b) $[FeCl_4]^{2-}$
(c) $[NiCl_4]^{2-}$ (d) $[PtCl_4]^{2-}$

Ans. ***(d)***

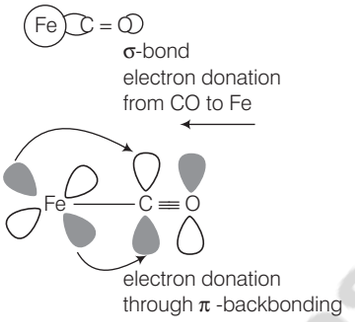
Cl^- is a weak ligand but Cl^- cause the pairing of electrons with large Pt^{2+} and consequently give dsp^2 hybridisation and square planar geometry.

124 In $Fe(CO)_5$, the Fe—C bond possesses **[AIEEE 2006]**

(a) π-character only
(b) both σ and π-characters
(c) ionic character
(d) σ-character only

Ans. ***(b)***

$Fe(CO)_5$ is an organometallic coordinated compound in which electrons from d-orbital of Fe are partially transferred to anti-bonding molecular oritals (π^*) of CO. This type of bonding is called π-backbonding.



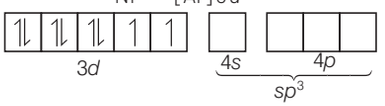
Thus, $Fe(CO)_5$ possesess both σ and π-character.

125 Nickel ($Z = 28$) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electron (s) in the nickel and geometry of this complex ion are, respectively **[AIEEE 2006]**

(a) one, tetrahedral
(b) two, tetrahedral
(c) one, square planar
(d) two, square planar

Ans. ***(b)***

$_{28}Ni = [Ar]4s^2, 3d^8$
$Ni^{2+} = [Ar]3d^8$



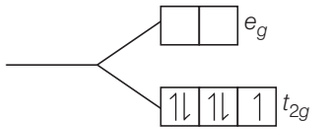
Nickel has two unpaired electrons and geometry is tetrahedral due to sp^3 hybridisation.

126 The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is **[AIEEE 2005]**

(a) d^5 (in strong ligand field)
(b) d^3 (in weak as well as in strong fields)
(c) d^4 (in weak ligand field)
(d) d^4 (in strong ligand field)

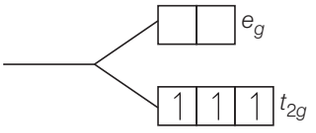
Ans. ***(d)***

(a) d^5 in strong field
n = unpaired electron = 1



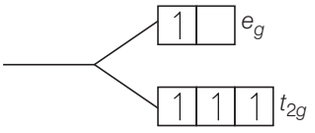
Magnetic moment $= \sqrt{n(n+2)}$ BM
$= \sqrt{3}$ BM $= 1.73$ BM

(b) d^3 in strong/weak field



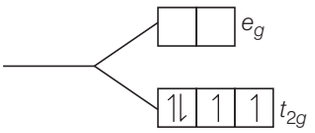
$n = 3$
Magnetic moment $= \sqrt{15} = 3.87$ BM

(c) d^4 in weak field



$n = 4$
Magnetic moment $= \sqrt{24} = 4.90$ BM

(d) d^4 in strong field



$n = 2$
Magnetic moment $= \sqrt{8} = 2.83$ BM

127 Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour ? **[AIEEE 2005]**
(At. no. of Cr = 24, Mn =25, Fe = 26, Co = 27)

(a) $[Co(CN)_6]^{3-}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Mn(CN)_6]^{3-}$ (d) $[Cr(CN)_6]^{3-}$

Ans. ***(a)***

	Hybridisation electrons	Unpaired moment	Magnetic
(a) $[Co(CN)_6]^{3-}$	d^2sp^3	(0)	0
(b) $[Fe(CN)_6]^{3-}$	d^2sp^3	(1)	$\sqrt{3}$ BM
(c) $[Mn(CN)_6]^{3-}$	d^2sp^3	(2)	$\sqrt{8}$ BM
(d) $[Cr(CN)_6]^{3-}$	d^2sp^3	(3)	$\sqrt{15}$ BM

Thus, least paramagnetism is (a).

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128 The correct order of magnetic moments (spin only values in BM) among the following is
(At. no of Mn = 25, Fe = 26, Co = 27)
[AIEEE 2004]

(a) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
(b) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
(c) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
(d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

Ans. ***(a)***

Number of unpaired electrons in $[Fe(CN)_6]^{4-}$ is zero.

Thus, magnetic moment

$= \sqrt{n(n+2)} = 0$ BM

(n = unpaired electrons)

n in $[MnCl_4]^{2-} = 5, \sqrt{35}$ BM

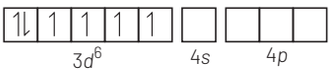
n in $[CoCl_4]^{2-} = 3, \sqrt{15}$ BM

129 Which one of the following complexes is an outer orbital complex? **[AIEEE 2004]**
(At. no. of Mn = 25, Fe = 26, Co = 27, Ni = 28)

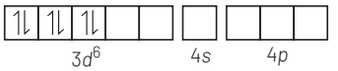
(a) $[Fe(CN)_6]^{4-}$ (b) $[Mn(CN)_6]^{4-}$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Ni(NH_3)_6]^{2+}$

Ans. ***(d)***

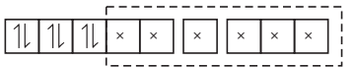
(a) $Fe^{2+} = [Ar]$



Fe^{2+} in strong ligand $CN^- = [Ar]$

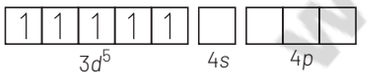


$[Fe(CN)_6]^{4-}$ [Ar]

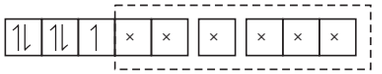


$d^2 sp^3$ (inner *d* orbital complex)

(b) $Mn^{2+} = [Ar]$

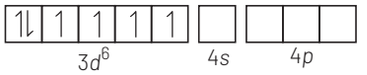


$[Mn(CN)_6^{4-}] = [Ar]$

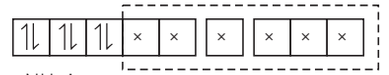


$d^2 sp^3$ (inner *d* orbital complex)

(c) $Co^{3+} = [Ar]$



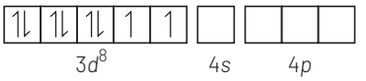
$[Co(NH_3)_6]^{3+} = [Ar]$



NH_3 is a strong ligand

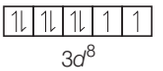
$d^2 sp^3$ (inner *d* orbital complex)

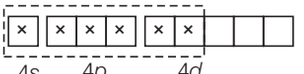
(d) $Ni^{2+} = [Ar]$



In this case also, NH_3 is a strong ligand but electrons remain unpaired, since only one orbital is left vacant in 3*d*. Thus, $[Ni(NH_3)_6]^{2+}$

[Ar]





sp^3d^2

(outer *d*-orbital complex)

130 The most stable ion is **[AIEEE 2002]**

(a) $[Fe(OH)_5]^{3-}$ (b) $[FeCl_6]^{3-}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$

Ans. ***(c)***

Stability of complex increases with increase in charge on the central metal ion and with increase in basic strength of ligand.

In $[Fe(CN)_6]^{3-}$, oxidation state of Fe is +3 and basicity of CN^- is higher than OH^-, Cl^- and H_2O.

TOPIC 3
Importance of Coordination Compounds

131 *Aqua-regia* is used for dissolving noble metals (Au, Pt, etc.). The gas evolved in this process is
[2020, 3 Sep Shift-I]

(a) NO (b) N_2O_5
(c) N_2 (d) N_2O_3

Ans. ***(a)***

Aqua-regia is a mixture of conc. HCl and conc. HNO_3 (3 : 1, *V* / *V*)

(i) $HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 \uparrow + 2H_2O$

(ii) $NOCl \longrightarrow NO \uparrow + [Cl]$

$\Rightarrow Pt(s) + 4[Cl] + 2HCl \longrightarrow H_2[PtCl_6](aq)$

$\Rightarrow Au(s) + 3[Cl] + HCl \longrightarrow \underset{\text{Soluble form}}{H[AuCl_4](aq)}$

Hence, the gas evolved in this process is NO.

132 The compound used in the treatment of lead poisoning is
[2019, 12 April Shift-II]

(a) D-penicillamine
(b) desferrioxime-B
(c) *cis*-platin
(d) EDTA

Ans. ***(d)***

The compound used in the treatment of lead poisoning is EDTA. Medication occurs through chelation therapy. Calcium disodium ethylenediamine tetraacetic acid chelates divalent metal ion such as Pb^{2+} from plasma and interstitial body fluids.

The metal displaces Ca and is chelated, mobilised and usually excreted. Less then 5% $CaNa_2$ EDTA is absorbed in the gastrointestinal tract and it possibly increases the absorption of Pb present in the tract. Therefore, it is not recommended for oral use. It is usually given intravenously.

133 Wilkinson catalyst is
[2019, 10 Jan Shift-I]

(a) $[(Et_3P)_3RhCl]$
(b) $[(Et_3P)_3IrCl]$ ($Et = C_2H_5$)
(c) $[(Ph_3P)_3RhCl]$
(d) $[(Ph_3P)_3IrCl]$

Ans. ***(c)***

Wilkinson's catalyst is a σ-bonded organometallic compound $[(Ph_3P)_3RhCl]$. It is commercially used for hydrogenation of alkenes and vegetable oils (unsaturated).

IUPAC name Chloridotris (triphenylphosphene) rhodium (I).

134 Coordination compounds have great importance in biological systems. In this context, which of the following statements is incorrect ? **[AIEEE 2004]**

(a) Chlorophyll is green pigment in plant and contain calcium
(b) Haemoglobin is the red pigment of blood and contains iron
(c) Cyanocobalamin is vitamin B_{12} and contains cobalt
(d) Carboxypeptidase-A is an enzyme and contains zinc

Ans. ***(a)***

Chlorophyll contains Mg, hence (a) is incorrect statement.

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20

Environmental Chemistry

TOPIC 1
Atmospheric Pollution

01 In stratosphere most of the ozone formation is assisted by

[2021, 27 Aug Shift-II]

(a) cosmic rays
(b) γ-rays
(c) ultraviolet radiations
(d) visible radiations

Ans. ***(c)***

In the stratosphere, the UV-light causes the splitting of O_2 molecule into oxygen atoms. These atoms react with oxygen present in the air to form ozone.

$$O_2(g) \xrightarrow{\text{UV radiation}} O(g) + O(g)$$

$$\xrightarrow{O_2(g) + \text{UV radiation}} \underset{\text{Ozone}}{O_3(g)}$$

Therefore, the option (c) is correct.

02 The gas '*A*' is having very low reactivity reaches to stratosphere. It is non-toxic and non-flammable but dissociated by UV-radiations in stratosphere. The intermediates formed initially from the gas '*A*' are

[2021, 27 Aug Shift-I]

(a) $\dot{C}lO + \dot{C}F_2Cl$ (b) $\dot{C}lO + \dot{C}H_3$
(c) $\dot{C}H_3 + \dot{C}F_2Cl$ (d) $\dot{C}l + \dot{C}F_2Cl$

Ans. ***(d)***

The gas is chlorofluoro carbon. Its reaction in stratosphere is as follows :

(i) $CCl_2F_2 + \text{UV light} \longrightarrow \dot{C}ClF_2 + \dot{C}l$

(ii) $CCl_3F + \text{UV light} \longrightarrow \dot{C}Cl_2F + Cl$

(iii) $Cl + O_3 \longrightarrow ClO + O_2$

(iv) $ClO + O \longrightarrow Cl + O_2$

So, the intermediate in first step are $\dot{C}l + \dot{C}ClF_2$.

03 Match List I with List II.

	List I (Compound)		List II (Effect/affected species)
A.	Carbon monoxide	I.	Carcinogenic
B.	Sulphur dioxide	II.	Metabolised by pyrus plants
C.	Polychlorinated biphenyls	III.	Haemoglobin
D.	Oxides of nitrogen	IV.	Stiffness of flower buds

Choose the correct answer from the options given below :

[2021, 27 July Shift-II]

	A	B	C	D		A	B	C	D
(a)	III	IV	I	II	(b)	IV	I	III	II
(c)	I	II	III	IV	(d)	III	IV	II	I

Ans. ***(a)***

A. If haemoglobin binds CO, it prevents the binding of O_2 to haemoglobin due to the competition for same binding sites.

B. Higher conc. SO_2 in air can cause stiffness of flower buds.

C. Polychlorinated biphenyls are carcinogenic (cancer causing) in humans as well as animals.

D. Certain plants, e.g. pinus, Juniparus, quercus, pyrus and vitis can metabolise nitrogen oxides.

Hence, the correct match is A → (III), B → (IV), C → (I), D → (II).

04 Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Photochemical smog causes cracking of rubber.

Reason (R) Presence of ozone, nitric oxide, acrolein, formaldehyde and peroxyacetyl nitrate in photochemical smog makes it oxidising.

Choose the most appropriate answer from the options given below. **[2021, 26 Aug Shift-II]**

(a) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(b) Both (A) and (R) are true and (R) is the correct explanation of (A).
(c) (A) is false but (R) is true.
(d) (A) is true but (R) is false.

Ans. ***(b)***

Both Assertion and Reason are true and Reason is the correct explanation of Assertion. Smog is a type of intense air pollution.

It is composed of nitrogen oxides, sulphur oxides, ozone, smoke and other particulates. Rubber is an organic compound and it is sensitive to number of chemical influences-oxidation, reduction etc. Excessive cracking of rubber products can be one of the indicators of the presence of atmospheric photochemical oxidants.

Excessive cracking of rubber is caused by atmospheric ozone formed in the photochemical smog formation process.

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05 Given below are two statements :

Statement I Chlorofluoro carbons break down by radiation in the visible energy region and release chlorine gas in the atmosphere which then reacts with stratospheric ozone.

Statement II Atmospheric ozone reacts with nitric oxide to give nitrogen and oxygen gases, which add to the atmosphere.

For the above statements choose the correct answer from the options given below :

[2021, 25 July Shift-II]

(a) Statement I is incorrect but statement II is true
(b) Both statement I and II are false
(c) Statement I is correct but statement II is false
(d) Both statement I and II are correct

Ans. ***(b)***

Chlorofluoro carbons are broken down by powerful UV radiation and releases chlorine free radical which reacts with ozone and start chain reaction.

$$CF_2Cl_2(g) \xrightarrow{UV} \dot{Cl}(g) + \dot{C}F_2Cl(g)$$

$$\dot{Cl}(g) + O_3(g) \longrightarrow \dot{Cl}O(g) + O_2(g)$$

$$\dot{Cl}O(g) + O(g) \longrightarrow \dot{Cl}(g) + O_2(g)$$

∴Statement (I) is incorrect.

Atmosphere ozone reacts with nitric oxide to produce nitrogen dioxide and oxygen.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

∴Statement (II) is also incorrect.

06 Which one of the following gases is reported to retard photosynthesis ?

[2021, 20 July Shift-II]

(a) CO (b) CFCs (c) CO_2 (d) NO_2

Ans. ***(d)***

From the given gases, NO_2 is the gas which damage the leaves of plants and retard the photosynthesis. Higher concentration of NO_2 damage the leaves of plants and retard the rate of photosynthesis.

07 The statements that are true.

(A) Methane leads to both global warming and photochemical smog.
(B) Methane is generated from paddy fields.
(C) Methane is a stronger global warming gas than CO_2.
(D) Methane is a part of reducing smog.

Choose the most appropriate answer from the options given below **[2021, 18 March Shift-I]**

(a) (A), (B), (C) only (b) (A) and (B) only
(c) (B), (C), (D) only (d) (A), (B), (D) only

Ans. ***(a)***

Methane leads to both global warming and photochemical smog.

Order of contribution of global warming gas

$CO_2 > CH_4 > CFC > O_3 > N_2O > H_2O$

- Methane is generated in large amounts from paddy fields. CH_4 is 40 times stronger greenhouse gas than CO_2.
- CO_2 can be absorbed by photosynthesis or by formation of acid rain etc., while no such activities are there for methane.
- It has more heating effects. Hence, methane is stronger global warming gas than CO_2.
- Methane is not a part of reducing smog.

Hence, statements (*A*), (*B*) and (*C*) are true.

08 Reducing smog is a mixture of **[2021, 17 March Shift-I]**

(a) smoke, fog and O_3
(b) smoke, fog and SO_2
(c) smoke, fog and $CH_2=CH—CHO$
(d) smoke, fog and N_2O_3

Ans. ***(b)***

Classical smog (reducing smog) occurs in cool humid climate, it is a mixture of smoke, fog and SO_2.

It is a reducing mixture/smog.

Reducing smog = smoke + fog + SO_2

Note Photochemical smog occurs in warm, dry and sunny climate. The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories. Photochemical smog has high concentration of oxidising agents and is therefore, called as oxidising smog.

09 The greenhouse gas/es is (are)

(A) carbon dioxide
(B) oxygen
(C) water vapour
(D) methane

Choose the most appropriate answer from the options given below. **[2021, 16 March Shift-II]**

(a) Only (A) and (C) (b) Only (A)
(c) (A), (C) and (D) (d) Only (A) and (B)

Ans. ***(c)***

Greenhouse gases are carbon dioxide, methane, water vapours, nitrous oxide, CFCs and ozone. The greenhouse effect is a natural process that warms the Earth's surface. When the Sun's energy reaches the Earth's atmosphere, some of it is reflected back to space and the rest is absorbed and re-radiated by greenhouse gases. The absorbed energy warms the atmosphere and the surface of the Earth.

10 The type of pollution that gets increased during the day time and in the presence of O_3 is **[2021, 16 March Shift-I]**

(a) reducing smog (b) oxidising smog
(c) global warming (d) acid rain

Ans. ***(b)***

Oxidising smog (photochemical smog) gets increased during the day time and in the presence of O_3.

It occurs in warm, dry and sunny climate. When fossil fuels are burnt, hydrocarbons (unburnt fuels) and nitric oxide (NO) are produced. Ozone reacts rapidly with the NO to generate NO_2.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Ozone is a toxic gas and both NO_2 and O_3 are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).

11 Given below are two statements.

Statement I The pH of rain water is normally ~ 5.6.

Statement II If the pH of rain water drops below 5.6, it is called acid rain.

In the light of the above statements, choose the correct answer from the options given below. **[2021, 25 Feb Shift-II]**

(a) Both statements I and II are true.
(b) Both statements I and II are false.
(d) Statement I is true but statement II is false.
(d) Statement I is false but statement II is true.

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Ans. ***(a)***

The pH of rain water is normally 5.6. If it pH drop below 5.6, it is called acid rain.

∴ Both statements are correct.

12 Given below are two statements:

Statement I An allotrope of oxygen is an important intermediate in the formation of reducing smog.

Statement II Gases such as oxides of nitrogen and sulphur present in troposphere contribute to the formation of photochemical smog.

In the light of the above statements, choose the correct answer from the options given below. **[2021, 25 Feb Shift-I]**

(a) Both statement I and statement II are true.
(b) Both statement I and statement II are false.
(c) Statement I is true but statement II is false.
(d) Statement I is false but statement II is true.

Ans. ***(d)***

Reducing smog is a mixture of smoke, fog and sulphur dioxide. Therefore, statement I is false.

Tropospheric pollutants such as nitrogen oxide and sulphur oxide contribute to the formation of photochemical smog. So, statement II is true.

13 The gas released during anaerobic degradation of vegetation may lead to **[2021, 24 Feb Shift-I]**

(a) acid rain
(b) global warming and cancer
(c) corrosion of metals
(d) ozone hole

Ans. ***(b)***

Methane (CH_4) gas is evolved due to anaerobic degradation of vegetation which causes global warming and cancer. It is a heat trapping gas that forces the planet to warm drastically and quickly.

14 The statement that is not true about ozone is **[2020, 2 Sep Shift-I]**

(a) in the stratosphere, CFCs release chlorine free radicals (Cl), which reacts with O_3 to give chlorine dioxide radicals
(b) in the atmosphere, it is depleted by CFCs
(c) in the stratosphere, it forms a protective shield against UV radiation.
(d) it is a toxic gas and its reaction with NO gives NO_2

Ans. ***(a)***

Statement (a) is not true whereas all the given statements are true.

In the stratosphere, CFCs release chlorine free radicals ($Cl^{\bullet}$) which reacts with O_3 to give chlorine monoxide ($ClO^{\bullet}$) radicals but not chlorine dioxide radicals.

15 Thermal power plants can lead to **[2020, 3 Sep Shift-I]**

(a) acid rain
(b) blue baby syndrome
(c) ozone layer depletion
(d) eutrophication

Ans. ***(a)***

Thermal power plants emit oxides of nitrogen (NO_2) and sulphur (SO_2) in the atmosphere which are converted into HNO_3 and H_2SO_4 respectively in the pressure of rain water (H_2O).

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

$$SO_2 + \frac{1}{2}O_2 + H_2O \longrightarrow H_2SO_4$$

Their presence in rain water becomes acidic (pH< 5.6) and it is called acid rain.

'Blue baby syndrome' is the condition due to poor oxygen transportation in the blood, resulting in blueness of the skin in babies.

Ozone layer depletion takes place due to the attack of chlorofluorocarbon (CFCs) to ozone molecules.

'Eutrophication' is associated with water pollution when huge quantities of phosphates and nitrates are released into aquatic ecosystem.

16 The incorrect statement(s) among (A) – (D) regarding acid rain is (are) :

(A) It can corrode water pipes.
(B) It can damage structures made up of stone.
(C) It cannot cause respiratory ailments in animals.
(D) It is not harmful for trees. **[2020, 3 Sep Shift-II]**

(a) (C) and (D)
(b) (A), (C) and (D)
(c) (C) only
(d) (A), (B) and (D)

Ans. ***(c)***

Statements (A), (B) and (D) are correct whereas (C) is incorrect. Corrected statement is as follows : Acid rain can cause health problems in people. It causes respiratory aliments in human being and animals.

17 Among the gases (A)-(E), the gases that cause greenhouse effect are : **[2020, 8 Jan Shift-I]**

(A) CO_2 (B) H_2O
(C) CFCs (D) O_2
(E) O_3

(a) (A), (B), (C) and (D)
(b) (A) and (D)
(c) (A), (B), (C) and (E)
(d) (A), (C), (D) and (E)

Ans. ***(c)***

CO_2, H_2O, CFCs and O_3 are green house gases. These gases trap the UV-radiations coming from the sun and heat up the earth. Thus, heating up of earth is called green house effect.

18 **Assertion (A)** Ozone is destroyed by CFCs in the upper stratosphere.

Reason (R) Ozone holes increase the amount of UV radiation reaching the earth. **[2019, 8 April Shift-I]**

(a) Assertion and Reason are incorrect.
(b) Assertion and Reason are both correct and the Reason is the correct explanation for the Assertion.
(c) Assertion and Reason are correct, but the Reason is not the explanation for the Assertion.
(d) Assertion is false, but the Reason is correct.

Ans. ***(c)***

Ozone is destroyed by CFCs in the upper stratosphere.

These compounds ultimately reach the stratosphere where they get broken down by powerful UV radiations and release chlorine free radical. The chlorine free radicals react with ozone and cause its depletion by converting it into chlorine monoxide radical and molecular oxygen.

$$CF_2Cl_2(g) \xrightarrow{h\nu} Cl(g) + \dot{C}F_2Cl(g)$$

$$CFCl_3(g) \xrightarrow{h\nu} CFCl_2(g) + \dot{C}l(g)$$

$$\dot{C}l(g) + O_3(g) \longrightarrow Cl\dot{O}(g) + O_2(g)$$

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Ozone holes increase the amount of UV radiation reaching the earth. These radiations can cause skin cancer, sunburns, ageing of skin.

19 Excessive release of CO_2 into the atmosphere results in **[2019, 9 April Shift-I]**

(a) formation of smog
(b) depletion of ozone
(c) polar vortex
(d) global warming

Ans. ***(d)***

The effect of release of CO_2 gas into atmosphere is global warming.

20 The layer of atmosphere between 10 km to 50 km above the sea level is called as **[2019, 9 April, Shift-II]**

(a) stratosphere (b) mesosphere
(c) thermosphere (d) troposphere

Ans. ***(a)***

The atmosphere between the heights 10 to 50 km above the sea level is stratosphere. Atmosphere is not of the same thickness at heights.

21 The regions of the atmosphere, where clouds form and where we live, respectively, are **[2019, 10 April, Shift-I]**

(a) stratosphere and stratosphere
(b) troposphere and troposphere
(c) troposphere and stratosphere
(d) stratosphere and troposphere

Ans. ***(b)***

The lowest region of atmosphere is troposphere which extends upto the height of 10 km (approx) from sea level. We live in the tropospheric region. It contains air, water vapour and dust which can form clouds with the help of strong air movement.

Above the troposphere, stratospheric region extends upto 50 km from sea level. It contains mainly N_2, O_2, O_3 and little water vapour. O_3 in the stratosphere absorbs 99.5% of the sun's harmful UV raditions and thus protects the lives on the earth.

22 Air pollution that occurs in sunlight is **[2019, 10 April, Shift-II]**

(a) acid rain (b) oxidising smog
(c) fog (d) reducing smog

Ans. ***(b)***

In sunlight oxidising smog or photochemical smog or Los-Angeles smog is formed. This smog is brown in colour. It occurs in warm, dry and sunny climate. In presence of sunlight, NO_x (N-oxides), O_2 and unburnt hydrocarbons of air combine to produce photochemical smog which mainly contains peroxyacetyl nitrate (PAN).

$$CH_3—\overset{\overset{O}{\|}}{C}—O—O—NO_2 \text{ (PAN)}$$

23 The correct set of species responsible for the photochemical smog is **[2019, 12 April Shift-I]**

(a) N_2, NO_2 and hydrocarbons
(b) CO_2, NO_2, SO_2 and hydrocarbons
(c) NO, NO_2, O_3 and hydrocarbons
(d) N_2, O_2, O_3 and hydrocarbons

Ans. ***(c)***

The correct set of species responsible for the photochemical smog is NO, NO_2, O_3 and hydrocarbons. Photochemical smog appears in warm, dry and sunny climate which are obtained by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides. Following reactions are involved during the formation of photochemical smog.

(i) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
(Originates from burning of fossil fuels)

(ii) $2NO(g) + O_2(g) \xrightarrow{\text{Sunlight}} 2NO_2(g)$

$NO_2(g) \xrightarrow{h\nu} NO(g) + [O]$
Nascent oxygen

(iii) $O(g) + O_2(g) \rightleftharpoons O_3(g)$
Reacts rapidly with NO

$O_3(g) + NO(g) \longrightarrow NO_2(g) + O_2(g)$
Brown gas (in high concentration form haze)

$3CH_4(g) + 2O_3(g) \longrightarrow 3CH_2{=}O(g)$
Formaldehyde
(Unburnt hydrocarbon)

$+ CH_2{=}CHCH{=}O + H_2O$
Acrolein

24 The primary pollutant that leads to photochemical smog is **[2019, 12 April Shift-II]**

(a) acrolein (b) nitrogen oxides
(c) ozone (d) sulphur dioxide

Ans. ***(b)***

The primary pollutant that leads to photochemical smog is nitrogen oxides. Burning of fossil fuels such as petrol and diesel in automobiles, reaction between nitrogen and oxygen and other such reactions result in a variety of pollutants, two main of which are hydrocarbons (unburnt fuel) and nitric oxide (NO).

$N_2(g) + O_2(g) \xrightarrow[\text{diesel engines}]{\text{In petrol and}} 2NO(g)$

When the concentration of these pollutants is sufficiently high, a chain reaction initiate because of the interaction of sunlight with oxides of nitrogen.

$2NO(g) + O_2(g) \xrightarrow{\text{Sunlight}} 2NO_2(g)$

$NO_2(g) \xrightarrow{h\nu} NO(g) + [O]$
Nascent oxygen

$O_3(g) + NO(g) \longrightarrow NO_2(g) + O_2(g)$
Brown gas

25 The pH of rain water, is approximately

(a) 7.5 (b) 6.5
(c) 5.6 (d) 7.0

[2019, 9 Jan Shift-II]

Ans. ***(c)***

In clean air, rain water picks up some acidic oxides like CO_2 and SO_2 (obtained from volcanic eruptions). These substance make the rain slightly acidic (pH = 5.6 – 6). But, when rain falls through polluted air, it consumes oxides of sulphur (SO_x) and oxides of nitrogen (NO_x), mists of HCl etc. They make the rain more acidic (called acid rain) of pH range 3.5 to 5.6.

26 The reaction that is not involved in the ozone layer depletion mechanism in the stratosphere is

(a) $CH_4 + 2O_3 \longrightarrow 3CH_2{=}O + 3H_2O$
(b) $ClO^{\bullet}(g) + O(g) \longrightarrow \dot{C}l(g) + O_2(g)$
(c) $HOCl(g) \xrightarrow{h\nu} \dot{O}H(g) + \dot{C}l(g)$
(d) $CF_2Cl_2(g) \xrightarrow{h\nu} \dot{C}l(g) + \dot{C}F_2Cl(g)$

[2019, 10 Jan Shift-II]

Ans. ***(a)***

CH_4 is not present in the stratosphere and also it cannot diffuse or escape into the stratosphere like freon-12 (CF_2Cl_2) from the atmosphere.

In the stratosphere, ozone layer depletion take place mainly by chlorofluorocarbons (CFCs) like CF_2Cl_2 and the mechanism of ozone layer depletion can be shown as:

(i) $CF_2Cl_2(g) \xrightarrow{h\nu} \dot{C}l(g) + \dot{C}F_2Cl(g)$
[Option, (d)]

(ii) $\dot{C}l(g) + O_3(g) \longrightarrow ClO^{\bullet}(g) + O_2$

(iii) $ClO^{\bullet}(g) + O(g) \longrightarrow Cl^{\bullet}(g) + O_2(g)$
[Option (b)]

(iv) $\dot{C}l(g) + H_2O(g)$
[Present in the stratosphere]
$\rightarrow HOCl(g) + H^{\bullet}(g)$

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(v) $HOCl(g) \xrightarrow{h\nu} \dot{O}H(g) + Cl^{\bullet}(g)$
[Option (c)]

$\Rightarrow$ One $Cl^{\bullet}$ can destroy or deplete 10^5 O_3 molecules.

As (i) reaction is involved in the formation of photochemical smog, not in ozone layer depletion. So, option (a) is correct.

27 Taj Mahal is being slowly disfigured and discoloured. This is primarily due to **[2019, 11 Jan Shift-II]**

(a) water pollution
(b) soil pollution
(c) global warming
(d) acid rain

Ans. ***(d)***

Acid rain (pH = 3.5 – 5.6) constitutes strong acids like HNO_3, H_2SO_4 and H_2SO_3 which slowly react with marble ($CaCO_3$) of Taj Mahal and make it disfigured and discoloured.

Here, $CaCO_3$ (marble) gets dissolved in acids.

$$CaCO_3(s) \xrightarrow[\text{(Acid rain)}]{2\,H^{\oplus}(aq)} Ca^{2+}(aq) + H_2O(l) + CO_2(g)\uparrow$$

28 The molecule that has minimum/no role in the formation of photochemical smog, is **[2019, 12 Jan Shift-I]**

(a) N_2 (b) $CH_2 = O$
(c) NO (d) O_3

Ans. ***(a)***

N_2 molecule has minimum role in the formation of photochemical smog. While $CH_2 = O$, O_3 and NO has major role. When fossil fuels are burnt, a variety of pollutants are emitted.

Two of them are hydrocarbons (unburnt) and NO. When these pollutants build upto high levels, a chain reaction occurs from their interaction with sunlight. The reactions involved in the formation of photochemical smog are as follows:

$$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g)$$
$$O(g) + O_2(g) \rightleftharpoons O_3(g)$$
$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

O_3 reats with unburnt hydrocarbons to produce chemicals such as formaldehyde, acrolein and PAN.

$$3CH_4 + 2O_3 \longrightarrow 3CH_2 = O + 3H_2O$$
$$+ CH_2 = CCH = O + CH_3\,\underset{\underset{O}{\|}}{COONO_2}$$
(PAN)

29 The compound that is not a common component of photochemical smog is

(a) CF_2Cl_2 (b) $H_3C-\underset{\underset{O}{\|}}{C}-OONO_2$
(c) $CH_2 = CHCHO$ (d) O_3

[2019, 12 Jan Shift-II]

Ans. ***(a)***

Freons or CFCs or chlorofluoro carbons, i.e. CF_2Cl_2 is not the common component of photochemical smog. This smog is produced as the result of tropospheric pollution while freons are the components of stratospheric pollution. These are infact considered as the major cause of ozone layer depletion.

30 The upper stratosphere consisting of the ozone layer protects us from the sun's radiation that falls in the wavelength region of **[2019, 12 Jan Shift-II]**

(a) 600-750 nm (b) 400-550 nm
(c) 0.8-1.5 nm (d) 200-315 nm

Ans. ***(d)***

Sun emits UV-radiations, which according to following EM categorisation have the wavelength range from 1 nm to 400 nm.

Type	Wavelength range
Radio wave	> 0.1 m
Microwave	0.1 m to 1 mm
Infrared wave	1 mm to 700 nm
Visible rays	700 nm to 400 nm
Ultraviolet rays	400 nm to 1 nm
X-rays	1 nm to 10^{-3} nm
Gamma rays	< 10^{-3} nm

Thus, option (d) with 200-315 nm range is the correct option.

31 **Assertion** (A) Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Reason (R) The reaction between nitrogen and oxygen requires high temperature. **[JEE Main 2015]**

(a) Both Assertion and Reason are correct and the reason is the correct explanation for the Assertion.
(b) Both Assertion and Reason are correct but the reason is not the correct explanation for the Assertion.
(c) The Assertion is incorrect but the Reason is correct.
(d) Both the Assertion and Reason are incorrect.

Ans. ***(a)***

Nitrogen is an inert gas because of the presence of strong bond. That's why although there is 78% N_2 in the atmosphere but nitrogen oxide in not formed under ordinary conditions.

But when temperature is high enough i.e. $\approx$ 2000 K, it reacts with oxygen to form nitrogen oxide.

$$N_2 + O_2 \xrightarrow{\approx 2000\,K} 2NO$$

Thus, Assertion and Reason are true and Reason is the correct explanation of the Assertion.

32 The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was **[JEE Main 2013]**

(a) Methylisocyanate
(b) Methylamine
(c) Ammonia
(d) Phosgene

Ans. ***(a)***

Methylisocyanate $CH_3-N=C=O$ (MIC gas) gas was leaked from the storage tank of the union carbide plant in Bhopal gas tragedy.

33 Identify the incorrect statement from the following **[AIEEE 2011]**

(a) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer
(b) Ozone absorbs the intense ultraviolet radiations of the sun
(c) Depletion of ozone layer is because of its chemical reactions with chlorofluoro alkanes
(d) Ozone absorbs infrared radiations

Ans. ***(d)***

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$O_3 + h\nu \longrightarrow O_2 + O$$
$$NO_2 + O \longrightarrow NO + O_2$$

(a) Net reaction $2O_3 + h\nu \longrightarrow 3O_2$
Thus, ozone layer is depleted by oxides of nitrogen.
Thus, (a) is correct statement.

(b) Ozone layer is a protective layer and absorbs harmful UV rays from the sun.
Thus, (b) is also correct statement.

(c) $Cl + O_3 \longrightarrow \dot{Cl}O + O_2$
$O_3 + h\nu \longrightarrow \dot{O} + O_2$

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$ClO + \dot{O} \longrightarrow Cl + \dot{O}_2$

Net reaction

$2O_3 + h\nu \longrightarrow 3O_2$

Thus, ozone layer is also depleted by reaction with freons.

Thus, (c) is also correct statement.

(d) It is a incorrect statement as ozone layer is permeable for UV rays.

Thus, correct answer is (d).

34 Identify the wrong statements in the following **[AIEEE 2008]**

(a) Chlorofluorocarbons are responsible for ozone layer depletion
(b) Green house effect is responsible for global warming
(c) Ozone layer does not permit infrared radiation from the sun to reach the earth
(d) Acid rain is mostly because of oxides of nitrogen and sulphur

Ans. ***(c)***

Ozone layer permits the infrared radiation to pass through but doesn't permit the higher range of ultraviolet radiation to pass through.

35 The smog is essentially caused by the presence of **[AIEEE 2004]**

(a) O_2 and O_3
(b) O_2 and N_2
(c) oxides of sulphur and nitrogen
(d) O_3 and N_2

Ans. ***(a)***

Smog is formed by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides.

Smog mainly contains higher concentration of Peroxyacetyl nitrate (PAN) formed by the reaction of NO_2, O_3 and unsaturated hydrocarbons.

$NO_2 \xrightarrow{h\nu} NO + O$

$O + O_2 \rightleftharpoons O_3$

$NO + O_3 \longrightarrow NO_2 + O_2$

$NO + O_3 +$ unsaturated hydrocarbons $\rightarrow$ PAN

36 When rain is accompanied by a thunderstorm, the collected rain water will have a pH value **[AIEEE 2003]**

(a) slightly lower than that of rain water without thunderstorm
(b) slightly higher than that when the thunderstorm is not there
(c) uninfluenced by occurrence of thunderstorm
(d) which depends on the amount of dust in air

Ans. ***(a)***

During thunderstorm, there is formation of NO which changes to NO and ultimately to HNO_3 (acidrain).

$N_2 + O_2 \longrightarrow NO \xrightarrow{O_2} NO_2$

$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$

[pH< 7]

TOPIC 2
Water and Soil Pollution

37 Water sample is called cleanest on the basis of which one of the BOD values given below **[2021, 1 Sep Shift-II]**

(a) 11 ppm (b) 15 ppm
(c) 3 ppm (d) 21 ppm

Ans. ***(c)***

BOD is the biological oxygen demand. Cleanest water sample will have BOD value equal to (SO_2) 3 ppm as clean water could have BOD value of less than 5 ppm.

38 BOD values (in ppm) for clean water (A) and polluted water (B) are expected respectively **[2021, 31 Aug Shift-I]**

(a) $A > 50, B < 27$ (b) $A > 25, B < 17$
(c) $A < 5, B > 17$ (d) $A > 15, B > 47$

Ans. ***(c)***

BOD value of clean water is less than 5 ppm.

So, $A < 5$

BOD value of polluted water is greater than 17 ppm.

So, $B > 17$

Thus, correct option is (c).

39 Which one of the following statements is not correct ? **[2021, 27 July Shift-I]**

(a) Eutrophication indicates that water body is polluted.
(b) The dissolved oxygen concentration below 6 ppm inhibits fish growth.
(c) Eutrophication leads to increase in the oxygen level in water.
(d) Eutrophication leads to anaerobic conditions.

Ans. ***(c)***

Statement (c) is not correct as eutrophication leads to decrease in oxygen level. Eutrophication means well nourished. It occur in following four simple steps:

- Lakes in many parts of the Earth have been severly eutrophied by sewage, agricultural industrial wastes.
- The contaminents are rich in nitrate and phosphate, spark the over growth of algae in water bodies.
- When algae forms, it blocks sunlight from entering water and user up oxygen. Eventually, water becomes oxygen depleted.
- Finally, this oxygen depleted water becomes a dead zone and can no longer support life.

40 Given below are two statements

Statement I Non-biodegradable wastes are generated by the thermal power plants.

Statement II Bio-degradable detergents leads to eutrophication.

In the light of the above statements, choose the most appropriate answer from the option given below. **[2021, 18 March Shift-II]**

(a) Both statements I and II are false.
(b) Statement I is true but statement II is false.
(c) Statement I is false but statement II is true.
(d) Both statements I and II are true.

Ans. ***(d)***

Non-biodegradable wastes are generated by the thermal power plants which produces fly ash. Detergents which are biodegradable causes problem called eutrophication, which kills aquatic life by deprieving it of oxygen.

Hence, both statements are true.

41 Which of the following statement(s) is (are) incorrect reason for eutrophication ?

A. Excess usage of fertilisers.
B. Excess usage of detergents.
C. Dense plant population in water bodies.
D. Lack of nutrients in water bodies that prevent plant growth.

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Choose the most appropriate answer from the options given below. **[2021, 17 March Shift-II]**

(a) Only A (b) Only C
(c) B and D (d) Only D

Ans. ***(d)***

Statement (D) is incorrect.

As eutrophication is the gradual increase in the concentration of phosphorus, nitrogen, and other plant nutrients in an aging aquatic ecosystem such as a lake. The productivity or fertility of such an ecosystem naturally increases as the amount of organic material that can be broken down into nutrients increases.

42 Given below are two statements.

Statement I The value of the parameter "Biochemical Oxygen Demand (BOD)" is important for survival of aquatic life.

Statement II The optimum value of BOD is 6.5 ppm.

In the light of the above statements, choose the most appropriate answer from the options given below. **[2021, 24 Feb Shift-II]**

(a) Statement I is false but statement II is true.
(b) Both statements are true.
(c) Statement I is true but statement II is false.
(d) Both statements are false.

Ans. ***(c)***

Statement I is true but statement II is false.

Clean water would have BOD value of less than
5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.
Hence, the value of parameter 'BOD' is important for survival of aquatic life but optimum value of BOD is 17 ppm or more.
So, statement II is incorrect.

43 The condition that indicates a polluted environment is **[2020, 5 Jan Shift-I]**

(a) pH of rain water to be 5.6
(b) eutrophication
(c) BOD value of 5 ppm
(d) 0.03% of CO_2 in the atmosphere

Ans. ***(b)***

In this process large quantities of phosphates and nitrates are released into water. It enables rapid growth of bacteria and algae in water and then microorganism use so much oxygen, enough oxygen in not left for other animals living in the water.

In eutrophication nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity. It indicates polluted environment.

44 Biochemical oxygen demand (BOD) is the amount of oxygen required (in ppm) **[2020 Jan Shift-II]**

(a) for the photochemical breakdown of waste present in 1 m^3 volume of a water body.
(b) for sustaining life in a water body.
(c) by anaerobic bacteria to breakdown inorganic waste present in a water body.
(d) by bacteria to breakdown organic waste in a certain volume of a water sample.

Ans. ***(d)***

B.O.D is defined as the amount of oxygen (ppm) required by bacteria to breakdown organic waste in certain volume of a water sample.

45 Which is wrong with respect to our responsibility as a human being to protect our environment? **[2019, 8 April Shift-I]**

(a) Restricting the use of vehicles
(b) Avoiding the use of floodlighted facilities
(c) Setting up compost tin in gardens
(d) Using plastic bags

Ans. ***(d)***

Using plastic bags is wrong with respect to responsibility as a human being to protect our environment. Plastic bags are non-biodegradable in nature. It remains in the environment as such and does not degraded by bacteria. If it is not disposed properly then it may lead serious threat to the environment. The activities that can be used to protect our environment are as follows:

- Restricting the use of vehicles.
- Avoiding the use of flood lighted facilities.
- Setting up compost tin in gardens.

46 The maximum prescribed concentration of copper in drinking water is **[2019, 8 April Shift-II]**

(a) 5 ppm (b) 0.5 ppm
(c) 0.05 ppm (d) 3 ppm

Ans. ***(d)***

According to W.H.O. and US environmental protection agency guidelines, maximum allowable concentration of metals in drinking water are as follows :

Metal	Maximum concentration (ppm or mg dm^{-3})
Cd	0.005
Mn	0.05 (option-c)
Al	0.2
Fe	0.2
Cu	3.0 (option-d)
Zn	5.0 (option-a)

47 The concentration of dissolved oxygen (DO) in cold water can go upto

(a) 14 ppm (b) 10 ppm
(c) 8 ppm (d) 16 ppm
[2019, 11 Jan Shift-I]

Ans. ***(b)***

Dissolved oxygen (DO) is the oxygen dissolved in water either from atmosphere or by photosynthesis. The lower the concentration of DO in a water sample, the more polluted is the water sample.

The concentration range of dissolved oxygen (DO) in cold water reaches upto 10 ppm, but that in normal water (at room temperature) is within 5 ppm.

48 A water sample has ppm level concentration of the following metals: Fe = 0.2; Mn = 5.0; Cu = 3.0; Zn = 5.0. The metal that makes the water sample unsuitable for drinking is **[2019, 9 Jan Shift-I]**

(a) Cu (b) Fe
(c) Mn (d) Zn

Ans. ***(c)***

For drinking water, the maximum recommended levels of some metals, set by European Environment Commission (EEC) is

Metal	Max. concentration in ppm
Zn	5
Mn	0.05
Fe	0.2
Cu	3

As the concentration of Mn in the given water sample is more than the recommended concentration. Thus, it makes water unsuitable for drinking.

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49 The condition for methemoglobinemia by drinking water is **[2019, 9 Jan Shift-II]**

(a) > 50 ppm nitrate
(b) > 50 ppm chloride
(c) > 50 ppm lead
(d) > 100 ppm sulphate

Ans. ***(a)***

According to EEC (European Environment Commission), excess of NO_3^- (> 50 ppm) in drinking water may lead to methemoglobinemia ('Blue baby syndrome'). It also may cause stomach-cancer.

50 Water filled in two glasses *A* and *B* have BOD values of 10 and 20, respectively. The correct statement regarding them, is **[2019, 10 Jan Shift-I]**

(a) *A* is more polluted than *B*
(b) *A* is suitable for drinking, wherease *B* is not
(c) Both *A* and *B* are suitable for drinking
(d) *B* is more polluted than *A*

Ans. ***(d)***

BOD is defined as the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water. Clean water or drinking water has a BOD value < 5 ppm.

So, water filled with *A*, BOD = 10 ppm is polluted and water filled with *B*, BOD = 20 ppm, is also polluted.

But, *B* is more polluted than *A*.

51 Peroxyacetyl nitrate (PAN), an eye irritant is produced by **[2019, 11 Jan Shift-I]**

(a) organic waste
(b) acid rain
(c) classical smog
(d) photochemical smog

Ans. ***(d)***

Molecular formula of peroxyacetyl nitrate (PAN) is $CH_3—\overset{\overset{O}{\|}}{C}—O—O—NO_2$. It is a secondary pollutant. It is present in photochemical smog (oxidising or Los Angeles smog). PAN is a powerful lachrymator or tear producer and it also causes breathing troubles.

52 Water samples with BOD values of 4 ppm and 18 ppm, respectively, are **[2019, 12 Jan Shift-I]**

(a) clean and clean
(b) highly polluted and clean
(c) highly polluted and highly polluted
(d) clean and highly polluted

Ans. ***(d)***

The amount of oxygen required by bacteria to break down the organic matter present in a certain value of a sample of water is called biochemical oxygen demand (BOD). The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically. Clean water would have BOD value of less than 5ppm whereas highly polluted water would have BOD value of 17 ppm or more.

BOD value of clean water = 4 ppm

BOD value of highly polluted water = 18 ppm.

53 A water sample has ppm level concentration of following anions : **[JEE Main 2017]**

$F^- = 10$
$SO_4^{2-} = 100$
$NO_3^- = 50$

The anion/anions that make/makes the water sample unsuitable for drinking is/are

(a) Only NO_3^-
(b) Both SO_4^{2-} and NO_3^-
(c) Only F^-
(d) Only SO_4^{2-}

Ans. ***(c)***

NO_3^- The maximum limit of nitrate (NO_3^-) in drinking water is 50 ppm and its source is fertilisers. If the maximum limit is increased in water it will cause methemoglobinemia (blue baby syndrome.)

SO_4^{2-} The maximum limit of sulphate (SO_4^{2-}) according to WHO is 500 pm and its sources are acid rain, industries. Excess SO_4^{2-} has laxative effect.

F^- The maximum limit of fluoride (F^-) is about 1.5 ppm. Its higher concentration converts enamel to more harder fluorapatite. Concentration (>2ppm) causes brown mottling of teeth and high concentration (>10 ppm) are harmful for bones and teeth.

$\therefore$ SO_4^{2-} (100 ppm) and NO_3^- (50 ppm) in water is suitable for drinking but the concentration of F^- (10 ppm) makes water unsuitable for drinking.

54 The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of **[JEE Main 2016]**

(a) lead (b) nitrate
(c) iron (d) fluoride

Ans. ***(b)***

This water is unsuitable for drinking due to high concentration of nitrate. In drinking water, maximum permissible concentration of

Lead $\simeq$ 50 ppb
Nitrate $\simeq$ 50 ppb
Iron $\simeq$ 0.2 ppm
Fluoride $\simeq$ 1 ppm

55 What is DDT among the following? **[AIEEE 2012]**

(a) Green house gas
(b) A fertilizer
(c) Biodegradable pollutant
(d) Non-biodegradable pollutant

Ans. ***(d)***

DDT is a non-biodegradable pollutant. It is the first chlorinated organic insecticide.

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21

Purification and Characterisation of Organic Compounds

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TOPIC 1
Methods of Purification

01 Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) A simple distillation can be used to separate a mixture of propanol and propanone.

Reason (R) Two liquids with a difference of more than 20°C in their boiling points can be separated by simple distillations.

In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 31 Aug Shift-I]

(a) (A) is false but (R) is true.
(b) Both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false
(d) Both (A) and (R) are correct and (R) is the correct explanation of (A).

Ans. ***(d)***

Propanol and propanone can be separated by simple distillation technique as difference in boiling point of propanol and propanone is more than 20°C.

Boiling point of propanol = 97°C.

Boiling point of propanone = 56°C

Difference in boiling points = 41° C > 20° C

Hence, option (d) is correct.

02 Which purification technique is used for high boiling organic liquid compound (decomposes near its boiling point)?

[2021, 22 July Shift-II]

(a) Simple distillation
(b) Steam distillation
(c) Fractional distillation
(d) Reduced pressure distillation

Ans. ***(d)***

Distillation under reduced pressure is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points.

Because the boiling point of liquids are decreased at reduced pressure. Organic compounds can be distilled at lower temperatures.

Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface.

By reducing pressure, it can be distilled at low boiling point to avoid their decomposition.

03 Given below are two statements.

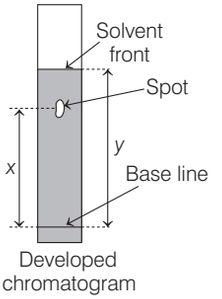
Statement I Retardation factor (R_f) can be measured in metre/centimetre.

Statement II R_f value of a compound remains constant in all solvents.

Choose the most appropriate answer from the options given below **[2021, 17 March Shift-I]**

(a) Statement I is true but statement II is false.
(b) Both statement I and statement II are true.
(c) Both statement I and statement II are false.
(d) Statement I is false but statement II is true.

Ans. ***(c)***



Developed chromatogram

$$R_f = \frac{\text{Distance moved by the substance from base line } (x)}{\text{Distance moved by the solvent from base line } (y)}$$

R_f (Retardation factor is dimensionless)

Different compounds are differently adsorbed in various.

So, R_f value of a compound varies with solvent and it is not constant.

Both statements I and II are false.

04 In chromatography technique, the purification of compound is independent of **[2021, 16 March Shift-I]**

(a) mobility or flow of solvent system
(b) solubility of the compound
(c) length of the column or TLC plate
(d) physical state of the pure compound

Ans. ***(d)***

In chromatography technique, the purification of compound is independent of physical state of the pure compound (stationary phase). Chromatography is based on the principle of adsorbtion. Different substances are differently adsorbed.

The technique of chromatography uses the difference in the rates at which the components of a mixture move through a porous medium (stationary phase) under the influence of some solvent or gas (moving phase).

05 Given below are two statements :

Statement I A mixture of chloroform and aniline can be separated by simple distillation.

Statement II When separating aniline from a mixture of aniline and water by steam distillation aniline boils below its boiling point.

In the light of the above statements, choose the most appropriate answer from the options given below. **[2021, 26 Feb Shift-I]**

(a) Statement I is false but statement II is true
(b) Both statement I and statement II are false
(c) Statement I is true but statement II is false
(d) Both statement I and statement II are true

Ans. ***(d)***

Statement I is true, i.e. a mixture of chloroform and aniline can be separated by simple distillation. Boiling points of chloroform (334 K) and aniline (457 K) differ largely. So, on boiling the mixture, vapours of $CHCl_3$ are formed first which is then condensed to pure liquid $CHCl_3$. Whereas, the vapours of aniline will form later and liquid aniline can be collected separately.

Statement II is also true, i.e. aniline and water can be separated by steam distillation technique. Aniline is steam volatile but immiscible with water. So, a mixture of aniline and water will boil close to but below 373 K. After distillation, the mixture of aniline (bottom layer) and water (top layer) can be separated by separating funnel.

So, both statements I and II are true (option-d).

06 Glycerol is separated in soap industries by **[2020, 3 Sep Shift-I]**

(a) fractional distillation
(b) differential extraction
(c) steam distillation
(d) distillation under reduced pressure

Ans. ***(d)***

In soap industries, glycerol is separated from spent lye using distillation under reduced pressure.

So, option (d) is correct.

(a) Fractional distillation is used to separate two liquids when difference in their boiling points is not much.
e.g. Separation of different fractions of crude oil in petroleum refinery.
(b) Differential extraction is based on different solubilities of an organic compound in different solvents. In this process same solvent is repeatedly used (continuous extraction) for extraction of the compound.
(c) Steam distillation method is used to separation substances which are steam volatile and are immiscible with water.
e.g. Separation of aniline water mixture.

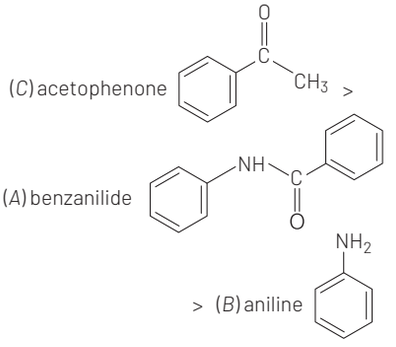
07 A chromatography column, packed with silica gel as stationary phase, was used to separate a mixture of compounds consisting of (*A*) benzanilide (*B*) aniline and (*C*) acetophenone. When the column is eluted with a mixture of solvents, hexane : ethyl acetate (20 : 80), the sequence of obtained compounds is **[2020, 7 Jan Shift-II]**

(a) (*C*), (*A*) and (*B*) (b) (*A*), (*B*) and (*C*)
(c) (*B*), (*C*) and (*A*) (d) (*B*), (*A*) and (*C*)

Ans. ***(a)***

In column chromatography, individual components of a mixture are separated by elution (washing with solvents). The component with relatively stronger rate of adsorption attached with mobile phase (solvents) move faster down the column (greater R_f value), and gets eluted first, followed by other components in the decreasing order of R_f values.

In the given separation, the solvent used has greater polarity due to greater composition of polar solvent ethyl acetate (80%), and therefore, more polar component (having greater dipole moment) of mixture will have more R_f value and will get eluted faster. Dipole moment of components in mixture is in the order :



∴ The sequence of obtained compounds is (*C*) > (*A*) > (*B*)

08 A flask contains a mixture of isohexane and 3-methylpentane. One of the liquids boils at 63°C while the other boils at 60°C. What is the best way to separate the two liquids and which one will be distilled out first? **[2020, 8 Jan Shift-I]**

(a) Fractional distillation 3-methylpentane
(b) Fractional distillation, isohexane
(c) Simple distillation, 3-methylpentane
(d) Simple distillation, isohexane

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Ans. ***(b)***

The boiling points of the given compounds are very close.

∴ Simple distillation can't be used.

Fractional distillation is only suitable to separate the two liquids.

Further, the liquid with lower boiling point distills out first. Since, 3-methyl pentane has a more symmetrical structure as compared to isohexane. Therefore, it has a greater area of contact and better interaction between molecules. This accounts for the greater boiling point of 3-methyl pentane as compared to isohexane.

Isohexane 60°C | 3-methyl pentane 63°C

09 The principle of column chromatography is

[2019, 10 April Shift-I]

(a) differential absorption of the substances on the solid phase
(b) differential adsorption of the substances on the solid phase
(c) gravitational force
(d) capillary action

Ans. ***(b)***

In column chromatography, separation of mixture of compounds (adsorbate) takes place over a column of solid adsorbent (silica gel and Al_2O_3) packed in a glass tube.

When an appropriate eluant (liquid) is allowed to flow down the column, the compounds present in the mixture get adsorbed to different extent on the adsorbent column and thus complete separation takes place.

Thus, column chromatography is based on the differential adsorption of the substance on the solid phase.

10 In chromatography, which of the following statements is incorrect for R_f?

[2019, 10 April Shift-II]

(a) R_f value depends on the type of chromatography
(b) Higher R_f value means higher adsorption
(c) R_f value is dependent on the mobile phase
(d) The value of R_f can not be more than one

Ans. ***(b)***

In chromatography, the expression of retention factor (R_f) is

$$R_f = \frac{\text{Distance travelled by the compound from origin}}{\text{Distance travelled by the solvent from origin}} < 1$$

The value of R_f signifies the relative ratio of migration of each component of the mixture with respect to the developing solvent used. R_f value depends on the type of adsorption chromatography like TLC (Thin-Layer Chromatography), paper chromatography etc. The R_f value is also the characteristic of a compound (sample) for a given developing solvent at a given temperature.

When the compound in the sample (usually less polar) is weakly adsorbed the spot will travel a shorter distance from the origin and hence the R_f value will be decreased.

11 If dichloromethane (DCM) and water (H_2O) are used for differential extraction, which one of the following statements is correct?

(a) DCM and H_2O would stay as lower and upper layer respectively in the S.F.
(b) DCM and H_2O would stay as upper and lower layer respectively in the separating funnel (SF)
(c) DCM and H_2O will be miscible clearly
(d) DCM and H_2O will make turbid/colloidal mixture

[2019, 10 Jan Shift-I]

Ans. ***(a)***

Dichloromethane, DCM (CH_2Cl_2) is heavier (density = 1.3266 g cm^{-3}) than water (density = 1g cm^{-3}). So, DCM and H_2O will stay as lower and upper layer respectively in the separating funnel (SF).

12 The correct match between items I and II is

[2019, 11 Jan Shift-I]

	Item I (Mixture)		Item II (Separation method)
A.	H_2O : Sugar	P.	Sublimation
B.	H_2O : Aniline	Q.	Recrystallisation
C.	H_2O : Toluene	R.	Steam distillation
		S.	Differential extraction

(a) (A)→(Q); (B)→(R); (C)→(S)
(b) (A)→(Q); (B)→(R); (C)→(P)
(c) (A)→(S); (B)→(R); (C)→(P)
(d) (A)→(R); (B)→(P); (C)→(S)

Ans. ***(a)***

The correct option is :
(A)→(Q); (B)→(R); (C)→(S)

(A) H_2O and sugar mixture They do not react chemically. On heating, solubility of sugar in H_2O increases and on rapid cooling of saturated solution, sugar recrystallises (*Q*).

(B) H_2O and aniline mixture Aniline is steam volatile but insoluble in H_2O. So, steam distillation (*R*) is employed for their separation.

(C) H_2O and toluene mixture Toluene is steam non-volatile and also insoluble in H_2O. So, differential extraction method (S) can be used to separate them.

13 The distillation technique most suited for separating glycerol from spent lye in the soap industry is

[JEE Main 2016]

(a) fractional distillation
(b) steam distillation
(c) distillation under reduced pressure
(d) simple distillation

Ans. ***(c)***

Glycerol with high boiling point (290°C) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points. By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.

TOPIC 2
Qualitative Analysis

14 The metal that can be purified economically by fractional distillation method is

[2021, 20 July Shift-I]

(a) Fe (b) Zn (c) Cu (d) Ni

Ans. ***(b)***

Zinc can be purified economically by fractional distillation.

Fractional distillation process utilises the boiling point difference between metal and that of impurity. Using this process, crude zinc containing Cd, Fe and Pb as impurities can be refined.

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15 In the sulphur estimation, 0.471 g of an organic compound gave 1.44 g of barium sulphate. The percentage of sulphur in the compound is ..... %.
(Nearest integer)
(Atomic mass of Ba = 137 u)
[2021, 26 Aug Shift-II]

Ans. ***(42)***

Atomic mass of sulphur is 32 g.
Molecular weight of $BaSO_4$ is 233 g.
So, weight of sulphur in $BaSO_4$

$$= \frac{\text{Atomic mass of sulphur}}{\text{Molecular weight of } BaSO_4} \times \text{Weight of } BaSO_4$$

$$= \frac{32}{233} \times 1.44$$

Percentage of sulphur

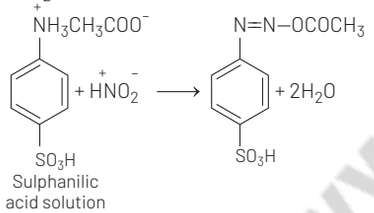
$$= \frac{\text{Weight of sulphur}}{\text{Weight of organic compound}} \times 100$$

$$= \frac{32}{233} \times \frac{1.44}{0.471} \times 100 = 41.98 \simeq 42\%$$

16 Reagent, 1-naphthylamine and sulphanilic acid in acetic acid is used for the detection of
[2021, 18 March Shift-I]
(a) N_2O (b) NO_3^- (c) NO (d) NO_2^-

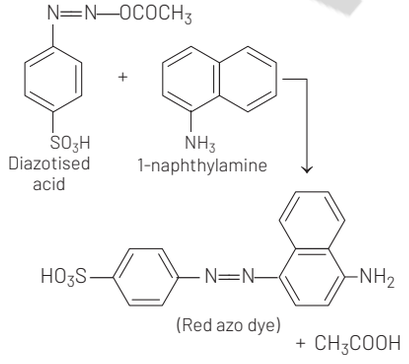
Ans. ***(d)***

When a solution is acidified with acetic acid, sulphanilic acid and then 1-naphthylamine is added, the red coloured precipitate obtain indicates presence of NO_2^- anions. For detection of NO_2^- following test is used.

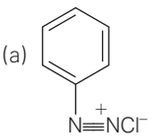


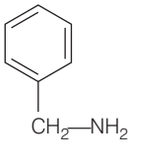
Sulphanilic acid solution

Above reagent is used to detect NO_2^- ion.

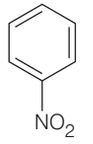


17 Nitrogen can be estimated by Kjeldahl's method for which of the following compound ?
[2021, 17 March Shift-II]

(a) 

(b) 

(c)

(d) 

Ans. ***(b)***

Nitrogen can be estimated by Kjeldahl's method for the benzyl amine as in this compound nitrogen is not the part of ring and is free to react.

Because this method can be readily applied to the compound in which nitrogen is free to react with the reagent. The compounds which have nitrogen in the ring (like pyridine), an azo compound, or in nitro compounds are not readily converted into the ammonium sulphate by the action of sulphuric acid.

18 Match the following :

	Test / Method		Reagent
I.	Lucas test	(A)	$C_6H_5SO_2Cl$/ KOH
II.	Dumas method	(B)	HNO_3 / $AgNO_3$
III.	Kjeldahl's method	(C)	CuO /CO_2
IV.	Hinsberg test	(D)	Conc. HCl and $ZnCl_2$
		(E)	H_2SO_4

[2020, 6 Sep Shift-II]
(a) (I)-(D), (II)-(C), (III)-(B), (IV)-(E)
(b) (I)-(B), (II)-(D), (III)-(E), (IV)-(A)
(c) (I)-(D), (II)-(C), (III)-(E), (IV)-(A)
(d) (I)-(B), (II)-(A), (III)-(C), (IV)-(D)

Ans. ***(c)***

Correct match is
I → (D), II → (C), III → (E), IV → (A)

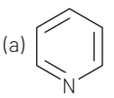
(I) Lucas test → Conc.HCl + $ZnCl_2$
It is a solution of anhydrous zinc chloride in concentrated hydrochloric acid. This solution is used to classify alcohols of low molecular weight. Primary, secondary and tertiary alcohols are classified based on their reactivity with the Lucas reagent.

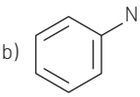
(II) Duma's method → CuO / CO_2
This method is based upon the fact that nitrogenous compound when heated with cupric oxide in an atmosphere of CO_2, yield free nitrogen. Traces of oxide of nitrogen, which may be formed in some cases, are reduced to elemental nitrogen by passing over heated copper spiral.

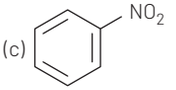
(III) Kjeldahl's method → H_2SO_4
This method is used for the quantitative determination of nitrogen containing organic substances. In this method, consists of heating a sample at 360-410°C with concentrated sulphuric acid (H_2SO_4), which decomposes the organic sample by oxidation to liberate the reduced nitrogen as ammonium sulphate.

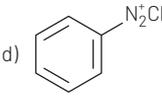
(IV) Hinsberg test →
$C_6H_5SO_2Cl$ / *aq*. KOH
Hinsberg reagent is an alternative name for benzene sulphonyl chloride.
This name is given for its use in the Hinsberg test for the detection and distinction of primary, secondary and tertiary amine in a given sample.
So, correct match is option (c).

19 Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation?
[JEE Main 2018]

(a) 

(b) 

(c) 

(d) 

Ans. ***(b)***

Estimation of nitrogen through Kjeldahl's method is not suitable for organic compounds containing nitrogen in ring or nitrogen in nitro or azo groups. It is because of the fact that nitrogen of these compounds does not show conversion to Ammonium sulphate ($(NH_4)_2SO_4$) during the process. Hence, among the given compounds only aniline can be used suitably for estimation of nitrogen by Kjeldahl's method.

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TOPIC 3
Quantitative Analysis

20 The transformation occurring in Duma's method is given below

$$C_2H_7N + \left(2x + \frac{y}{2}\right)CuO \longrightarrow x\,CO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$$

The value of *y* is ..... . (Integer answer) **[2021, 31 Aug Shift-II]**

Ans. ***(7)***

For the reaction

$$C_2H_7N + \left(2x + \frac{y}{2}\right)CuO \longrightarrow x\,CO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$$

On reactant side number of H-atom = 7

On product side number of H-atom

$$= \frac{y}{2} \times 2$$

$$7 = \frac{y}{2} \times 2$$

$$\therefore \quad y = 7$$

21 The number of moles of CuO, that will be utilised in Dumas method for estimation nitrogen in a sample of 57.5 g of N, N-dimethylaminopentane is ..... $\times 10^{-2}$. (Nearest integer) **[2021, 27 Aug Shift-I]**

Ans. ***(1125)***

In Dumas method,

$$C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2} + \left(2x + \frac{y}{2}\right)Cu$$

N,N-dimethylaminopentane has formula $C_7H_{17}N$.

So, relating with $C_xH_yN_z$

$$x = 7;\ y = 17;\ z = 1$$

Molar mass of $C_7H_{17}N = 115$ g

1 mole $C_7H_{17}N$ requires $= \left(2x + \frac{y}{2}\right)CuO$

$= 22.5$ moles of CuO

57.5 g i.e. $\left(\frac{57.5}{115}\right)C_7H_{17}N$ will utilise

$$= \frac{22.5}{115} \times 57.5 \text{ moles of CuO}$$

$= 11.25$ g mol

$\approx 1125 \times 10^{-2}$ mol.

22 In carius method for estimation of halogens, 0.2 g of an organic compound gave 0.188 g of AgBr. The percentage of bromine in the compound is ..... (Nearest integer)

[Atomic mass; Ag = 108, Br = 80] **[2021, 27 Aug Shift-I]**

Ans. ***(40)***

Mass of bromine = 80 u

Mass of silver = 108 u

Mass of AgBr = 108 + 80 = 188 u

Weight of organic compound = 0.2 g

$$\% \text{ of Br} = \frac{\text{Molar mass of Br}}{\text{Molar mass of AgBr}} \times \frac{\text{Weight of AgBr}}{\text{Weight of organic compound}} \times 100$$

$$= \frac{80}{188} \times \frac{0.188}{0.2} \times 100 = 40\%.$$

23 0.8 g of an organic compound was analysed by Kjeldahl's method for the estimation of nitrogen. If the percentage of nitrogen in the compound was found to be 42%, then ..... mL of 1 M H_2SO_4 would have been neutralised by the ammonia evolved during the analysis. **[2021, 25 July Shift-II]**

Ans. ***(12)***

Organic compound analysed by Kjeldahl's method = 0.8 g

$$\text{Weight of nitrogen} = \left(\frac{42}{100} \times 0.8\right)\text{g}$$

$$\text{Mole of N} = \frac{\text{weight of N}}{\text{molar mass of N}}$$

$$\text{Mole of N} = \frac{42 \times 0.8}{100 \times 14} = \frac{2.4}{100} \text{ mol}$$

$$\text{Mole of } NH_3 = \frac{2.4}{100} \text{ mol}$$

Reaction,

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$\frac{2.4}{100} \text{ mol} \quad \frac{1.2}{100} \text{ mol}$$

$\therefore$ 2 moles of NH_3 will neutralise 1 mole of H_2SO_4.

Given 1 M H_2SO_4 is neutralised by NH_3

$\therefore$ Molarity of

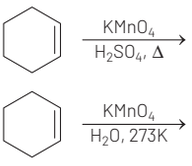
$$H_2SO_4 = \frac{\text{Moles of } H_2SO_4}{\text{Volume of solution (L)}}$$

$$1\,M = \frac{1.2}{100} \times \frac{1}{V_{H_2SO_4}(L)}$$

$$\therefore \text{ Number of mole of } H_2SO_4 = \frac{1 \cdot 2}{100}$$

$$V_{H_2SO_4} = \frac{1.2}{100} L \ \{1 L = 1000 mL\}$$

$$V_{H_2SO_4} = 12 mL$$

24 

For above chemical reactions, identify the correct statement from the following **[2021, 20 July Shift-I]**

(a) Both compound '*A*' and compound '*B*' are dicarboxylic acids.

(b) Both compound '*A*' and compound '*B*' are diols.

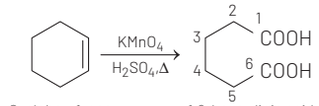
(c) Compound '*A*' is diol and compound '*B*' is dicarboxylic acid.

(d) Compound '*A*' is dicarboxylic acid and compound '*B*' is diol.

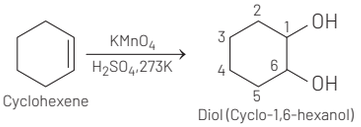
Ans. ***(d)***

Compound '*A*' is dicarboxylic acid and compound '*B*' is 'diol'. Alkenes forms dicarboxylic acid on treating with hot acidic $KMnO_4$.

Chemical reactions are as follows



Alkenes on treating with $KMnO_4$ in water at room temperature gives diol.



25 Methylation of 10 g of benzene gave 9.2 g of toluene. Calculate the percentage yield of toluene ..... . (Nearest integer) **[2021, 22 July Shift-II]**

Ans. ***(78)***

For the reaction,

$$C_6H_6(10g) + CH_3Cl + \text{Anhyd. } AlCl_3 \longrightarrow C_6H_5CH_3(9.2\ g)$$

1 mole of benzene produced 1 mole of toluene, if reaction yield is 100%.

78 g of benzene produced 92 g of toluene, if reaction yield is 100%.

$$\% \text{ yield} = \frac{\text{Actual yield}}{100\% \text{ yield}} \times 100$$

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$$\% \text{ yield} = \frac{9.2}{\frac{92}{78} \times 10} \times 100 = 78\%$$

Hence, % yield of toluene is 78.

26 When 0.15 g of an organic compound was analysed using Carius method for estimation of bromine, 0.2397 g of AgBr was obtained. The percentage of bromine in the organic compound is ..... . (Nearest integer)

[Atomic mass : Silver = 108, bromine = 80] **[2021, 20 July Shift-II]**

Ans. ***(68)***

Carius halogen method is generally used to determine the quantity of halogens in a chemical compound. In this method, heat known mass of an organic compound with fuming HNO_3 in presence of $AgNO_3$ in a hard glass tube.

Moles of Br = Moles of AgBr obtained

$$\text{Mass of Br} = \frac{\text{Mass of AgBr}}{\text{Molecular weight of AgBr}} \times \text{Molecular weight of Br}$$

$$= \frac{0.2397}{188} \times 80 \text{ g}$$

$$\% \text{ of Br} = \frac{w_{Br}}{w_{Total}} \times 100$$

$$= \frac{0.2397 \times 80}{188 \times 0.15} \times 100 = 0.85 \times 80 = 68$$

27 In Carius method, halogen containing organic compound is heated with fuming nitric acid in the presence of **[2021, 20 July Shift-II**

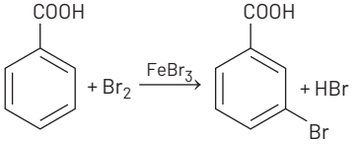
(a) HNO_3 (b) $AgNO_3$
(c) $CuSO_4$ (d) $BaSO_4$

Ans. ***(b)***

Organic compound is heated with fuming nitric acid in the presence of silver nitrate in Carius method.

This method used for quantitative determination of halogens in chemical substance. Method is based on the fact that when organic compound containing halogen (Cl, Br, I) is heated in sealed tube with fuming HNO_3 in presence of excess of $AgNO_3$, silver halide is formed.

28



Consider the above reaction where 6.1 g of benzoic acid is used to get 7.8 g of *m*-bromo benzoic acid. The percentage yield of the product is ..... .

(Round off to the nearest integer).

[Given : Atomic masses : C = 12.0 u, H = 1.0 u, O = 16.0u, Br = 80.0 u] **[2021, 18 March Shift-II]**

Ans. ***(78)***

Moles of benzoic acid

$$= \frac{6.1}{122} \frac{\text{(weight)}}{\text{(molecular weight)}}$$

= moles of *m*-bromobenzoic acid

So, weight of *m*-bromobenzoic acid

$$= \frac{6.1}{122} \times 201 \text{ g}$$

$$= 10.05 \text{ g}$$

$$\% \text{ yield} = \frac{\text{Actual weight}}{\text{Theoretical weight}} \times 100$$

$$= \frac{7.8}{10.05} \times 100 = 77.61\% \simeq 78\%$$

29 ..... grams of 3-hydroxy propanal (MW = 74) must be dehydrated to produce 7.8 g of acrolein (MW= 56) (C_3H_4O), if the percentage yield is 64 (Round off to the nearest integer).

[Given : Atomic masses : C = 12.0 u, H = 1.0 u, O = 16.0 u] **[2021, 18 March Shift-I]**

Ans. ***(16)***

On reaction

$$\underset{\substack{\text{3-hydroxy propanal}\\(\text{mol. wt} = 74)}}{HO{-}CH_2{-}CH_2{-}CHO} \xrightarrow[64\%]{\Delta} \underset{\substack{\text{Acrolein}\\(\text{mol. wt}=56)}}{C_3H_4O} + H_2O$$

Let's assume required man of 3-hydroxypropanal be *x* to produce 0.64 g acrolein.

$\therefore$ Number of moles = $x/74$

So, $\frac{x}{74}$ mol gives 0.64 g yield.

Now, 7.8 g of acrolein gives,

$$\frac{x}{74} \times 0.64 = \frac{7.8}{56}$$

$$\Rightarrow \quad x = 16.10 \text{ or } x \cong 16.00$$

30 A reaction of 0.1 mole of benzylamine with bromomethane gave 23 g of benzyl trimethyl ammonium bromide. The number of moles of bromomethane consumed in this reaction are $n \times 10^{-1}$, when n = ... (Round off to the nearest integer).

(Given : Atomic masses : C = 12.0 u, H = 1.0 u, N = 14.0 u, Br = 80.0 u] **[2021, 18 March Shift-I]**

Ans. ***(3)***

Benzylamine reacts with bromoethane to produce benzyltrimethyl ammonium bromide.

The reaction is as follows :

$$\underset{\substack{\text{Benzyl amine}\\(0.1 \text{ mol})}}{PhCH_2{-}NH_2} \xrightarrow[-HBr]{(i)\, CH_3Br} PhCH_2{-}\ddot{N}H{-}CH_3$$

$$PhCH_2{-}\ddot{N}H{-}CH_3 \xrightarrow[-HBr]{(ii)\, CH_3Br} \underset{\substack{\text{Benzyl trimethyl ammonium}\\\text{bromide (23 g)}}}{\left[Ph{-}CH_2{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}{-}CH_3\right] Br^-} \xleftarrow[-HBr]{(iii)\, CH_3Br}$$

$$Ph{-}CH_2{-}\ddot{N}(CH_3)_2$$

$$\underset{0.1 \text{ mol}}{Ph{-}CH_2NH_2} + 3CH_3Br \longrightarrow \underset{\frac{w}{m} = \frac{23g}{230} = 0.1 \text{ mol}}{PhCH_2\overset{+}{N}(Me)_3Br^-}$$

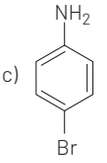
$$\Rightarrow \qquad 0.1 \times 3 = 0.3$$

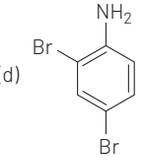
Total moles of $CH_3Br = 0.3$

$$= 3 \times 10^{-1} \text{ mol.}$$

31 In Carius method of estimation of halogen 0.172 g of an organic compound showed presence of 0.08 g of bromine. Which of these is the correct structure of the compound? **[2020, 2 Sep Shift-I]**

(a) $H_3C{-}Br$ (b) $H_3C{-}CH_2Br$

(c) 

(d) 

Ans. ***(c)***

In the organic compound

$$\text{Br}\% = \frac{0.08}{0.172} \times 100 = 46.51$$

Now, let us calculate Br % in the given compounds.

(a) CH_3Br ($M = 95$)

$$\Rightarrow \text{Br}\% = \frac{80}{95} \times 100 = 84.21$$

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(b) C_2H_5Br ($M = 109$)

$$\Rightarrow Br\% = \frac{80}{109} \times 100 = 73.39$$

(c) C_6H_6NBr ($M = 172$)

$$\Rightarrow Br\% = \frac{80}{172} \times 100 = 46.51$$

(d) $C_6H_5NBr_2$ ($M = 251$)

$$\Rightarrow Br\% = \frac{160}{251} \times 100 = 63.74$$

So, correct structure of compound is (c).

32 In an estimation of bromine by Carius method, 1.6 g of an organic compound gave 1.88 g of AgBr. The mass percentage of bromine in the compound is ..... . (Atomic mass, Ag = 108, Br = 80 g mol^{-1}) **[2020, 6 Sep Shift-I]**

Ans. ***(50)***

Molar mass of AgBr = 108 + 80 ⇒ 188 g/mol

Weight of organic compound = 1.6 g

Weight of AgBr = 1.88 g

$$\% \text{ of Br} = \frac{\text{Weight of AgBr} \times 80}{\text{Weight of organic compound} \times 188} \times 100$$

$$= \frac{1.88 \times 80}{1.6 \times 188} \times 100 = 50\%$$

Hence, the correct answer is 50.

33 An organic compound is estimated through Dumas method and was found to evolved 6 moles of CO_2, 4 moles of H_2O and 1 mole of nitrogen gas. The formula of the compound is **[2019, 11 Jan Shift-I]**

(a) C_6H_8N (b) $C_{12}H_8N$
(c) $C_{12}H_8N_2$ (d) $C_6H_8N_2$

Ans. ***(d)***

In Dumas method, organic compound is heated with dry cupric oxide in a combustion tube in the atmosphere of CO_2. Upon heating, C and H present are oxidised to CO_2 and water vapours while N_2 is set free.

Let, the molecular formula of the organic compound (1 mol) be $C_xH_yN_z$. In Dumas method,

$$\underset{1\text{ mol}}{C_xH_yN_z} + \left(2x + \frac{y}{2}\right)CuO \rightarrow xCO_2$$

$$x \text{ mol} \quad \frac{y}{2} \text{ mol} \quad \frac{z}{2} \text{ mol}$$

$$+ \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$$

Now, $x = 6, \frac{y}{2} = 4 \Rightarrow y = 8$ and $\frac{z}{2} = 1$

$$\Rightarrow \quad z = 2$$

∴ Molecular formula of the compound is $C_6H_8N_2$.

34 In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (at. mass Ag = 108, Br = 80) **[JEE Main 2015]**

(a) 24 (b) 36
(c) 48 (d) 60

Ans. ***(a)***

Given, Weight of organic compound = 250 mg

Weight of AgBr = 141 mg

∴ According to formula of % of bromine by Carius method

$$\% \text{ of Br} = \frac{\text{Atomic weight of Br}}{\text{Molecular weight of Ag Br}} \times \frac{\text{Weight of AgBr}}{\text{Weight of organic bromide}} \times 100$$

$$\therefore \% \text{ of Br} = \frac{80}{188} \times \frac{141}{250} \times 100$$

$$= \frac{1128000}{47000}$$

$$= 24\%$$

35 For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl's method and the evolved ammonia was absorbed in 60 mL of $M/10$ sulphuric acid. The unreacted acid required 20 mL of $M/10$ sodium hydroxide for the complete neutralization. The percentage of nitrogen in the compound is **[JEE Main 2014]**

(a) 6% (b) 10%
(c) 3% (d) 5%

Ans. ***(b)***

Mass of an organic compound (OC) = 1.4 g

Suppose x m mole of N-atom is present in organic compound. Thus,

$$\text{Organic compound} \xrightarrow[\text{method}]{\text{Kjeldahl's}} \underset{x \text{ m mole}}{NH_3}$$

Initial m mol of $H_2SO_4 = 60 \times \frac{M}{10} = 6$ mmol

mmoles of NaOH required by

$$H_2SO_4 = 20 \times \frac{M}{10} = 2 \text{ mmol}$$

Involved reactions are

$$2NH_3 + \underset{\left(\substack{6 \text{ mmol} \\ \text{Initially taken}}\right)}{H_2SO_4} \longrightarrow (NH_4)_2SO_4$$

$$H_2SO_4 + \underset{2 \text{ mmol reacted}}{2NaOH} \longrightarrow Na_2SO_4 + 2H_2O$$

Hence, 1 mmole of H_2SO_4 reacted with NaOH.

⇒ mmoles of H_2SO_4 reacted from first equation = 6 – 1 = 5 mmoles

⇒ mmoles of NH_3 in first equation = 2 × 5 = 10 mmoles

⇒ mmoles of N atoms in the organic compound = 10 m moles

$$\Rightarrow \text{ mass of N} = 10 \times 10^{-3} \times 14$$

$$= 0.14 \text{ g \% of N in}$$

$$\text{OC} = \frac{\text{Mass of N in OC}}{\text{Total mass of OC}} \times 100$$

$$\therefore \quad \% \text{ of N} = \frac{0.14}{1.4} \times 100 = 10\%$$

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22

Some Basic Principles of Organic Chemistry

TOPIC 1
Nomenclature

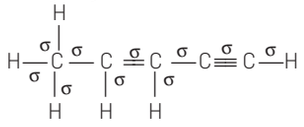
01 The number of sigma bonds in

is ..... .

[2021, 25 July Shift-I]

Ans. ***(10)***

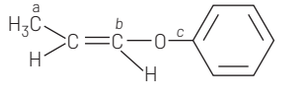
According to given structure,



Total number of σ bonds = 10

Note Double bond or triple bond contains one σ-bond and 2pi-bonds, respectively.

02 In the following molecules,



hybridisation of carbon *a*, *b* and *c* respectively are

[2021, 18 March Shift-II]

(a) sp^3, sp, sp (b) sp^3, sp^2, sp

(c) sp^3, sp^2, sp^2 (d) sp^3, sp, sp^2

Ans. ***(c)***

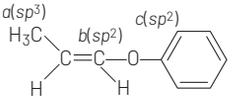
Hybridisation of carbon *a*, *b* and *c* respectively are sp^3, sp^2 and sp^2.

Here, *a* = carbon is sp^3 hybridised with 3 H atoms,

b = carbon is sp^2 hybridised with C ═ C,

c = carbon is sp^2 hybridised within benzene ring as C ═ C.

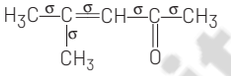
Structure is as follows



03 The total number of C—C sigma bond/s in mesityl oxide ($C_6H_{10}O$) is ..... . (Round off to the nearest integer). **[2021, 17 March Shift-II]**

Ans. ***(5)***

The structural formula with C—C sigma bond(s) in mesityl oxide is as follows:



Therefore, number of C—C sigma bonds in mesityl oxide = 5.

04 Mesityl oxide is a common name of **[2021, 17 March Shift-I]**

(a) 2,4-dimethyl pentan-3-one

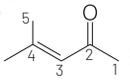
(b) 3-methyl cyclohexane carbaldehyde

(c) 2-methyl cyclohexanone

(d) 4-methyl pent-3-en-2-one

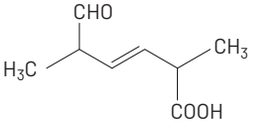
Ans. ***(d)***

Mesityl oxide is a common name of 4-methyl pent-3-en-2-one.



(4-methyl pent-3-en-2-one)

05 The IUPAC name for the following compound is



[2020, 2 Sep Shift-I]

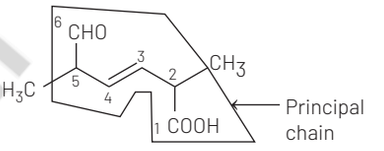
(a) 6-formyl-2-methyl-hex-3-enoic acid

(b) 2, 5-diamethyl-6-oxo-hex-3-enoic acid

(c) 2, 5-dimethyl-6-carboxy-hex-3-enal

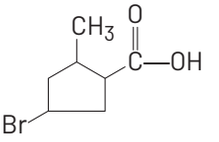
(d) 2, 5-dimethyl-5-carboxy-hex-3-enal

Ans. ***(b)***



IUPAC name is 2, 5-dimetyl-6-oxo-3-enoic acid.

06 The IUPAC name of the following compound is



[2020, 4 Sep Shift-I]

(a) 3-bromo-5-methylcyclopentane carboxylic acid

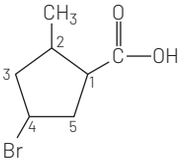
(b) 3-bromo-5-methylcyclopentanoic acid

(c) 5-bromo-3-methylcyclopentanoic acid

(d) 4-bromo-2-methylcyclopentane carboxylic acid

Ans. ***(d)***

The IUPAC name of the given compound.



4-bromo-2-methylcyclopentane carboxylic acid.

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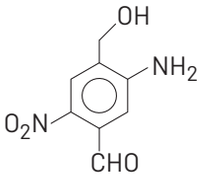
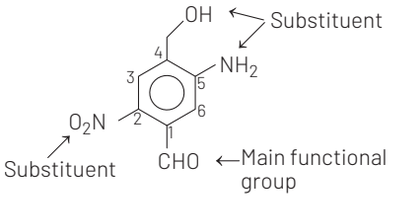
07 The IUPAC name of the following compounds is



[2020, 6 Sep Shift-II]

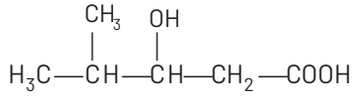
(a) 2-nitro-4-hydroxymethyl-5-amino benzaldehyde
(b) 3-amino-4-hydroxymethyl-1-5-nitrobenzaldehyde
(c) 5-amino-4-hydroxymethyl 1-2-nitrobenzaldehyde
(d) 4-amino-2-formyl -5-hydroxymethyl -nitrobenzene

Ans. *(c)*



5-amino-4-hydroxymethyl-1-2-nitrobenzal dehyde

08 The IUPAC name of the following compound is

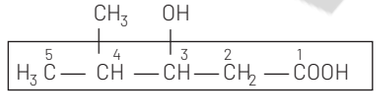


[2019, 8 April Shift-I]

(a) 4,4 - dimethyl -3-hydroxybutanoic acid
(b) 2-methyl-3-hydroxypentan-5-oic acid
(c) 3- hydroxy -4- methylpentanoic acid
(d) 4-methyl-3-hydroxypentanoic acid

Ans. *(c)*

The IUPAC name of the given compound is 3-hydroxy-4-methylpentanoic acid.

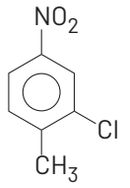


Principal chain

While naming the compound, the longest chain that have principal functional group —COOH is choosen and numbered in such a manner that the principal functional group gets the lowest possible number. —OH act as substituent and used as prefix in nomenclature.

09 The correct IUPAC name of the following compound is

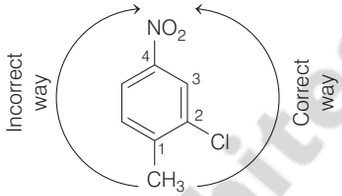
[2019, 9 April Shift-I]



(a) 2-methyl-5-nitro-1 -chlorobenzene
(b) 3-chloro-1-methyl-1-nitrobenzene
(c) 2-chloro-1-methyl 1-4-nitrobenzene
(d) 5-chloro-4-methyl 1-1-nitrobenzene

Ans. *(c)*

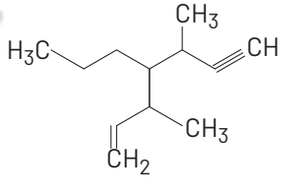
The IUPAC name of the given compound is



2- chloro-1-methy l-4-nitrobenzene

Here, the given compound contains two or more functional groups. So, the numbering is done in such a way that the sum of the locants is the lowest.

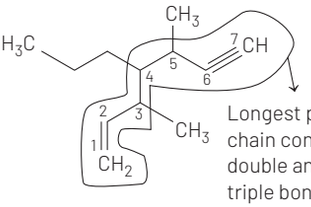
10 The IUPAC name for the following compound is **[2019, 12 April Shift-II]**



(a) 3-methyl-4-(3-methylprop-1-enyl)-1-heptyne
(b) 3, 5-dimethyl-4-propylhept-6-en-1-yne
(c) 3-methyl-4-(1-methylprop-2-ynyl)-1-heptene
(d) 3, 5-dimethyl-4-propylhept-1-en-6-yne

Ans. *(d)*

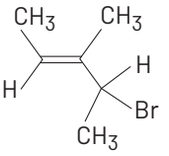
The IUPAC name for the given compound is 3, 5-dimethyl-4-propylhept-1-en-6-yne.



Longest possible chain containing double and triple bond

If both double and triple bonds are present in the compound, the endings like-en-yne, a (numeral) dien-(numeral)-yne etc., are used. Numbers as low as possible are given to double and triple bonds as a set.

11 What is the IUPAC name of the following compound ?

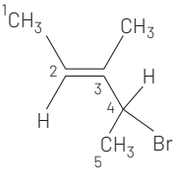


[2019, 10 Jan Shift-II]

(a) 3-bromo-3-methyl-1, 2-dimethylprop-1-ene
(b) 3-bromo-1,2-dimethylbut-1-ene
(c) 2-bromo-3-methylpent-3-ene
(d) 4-bromo-3-methylpent-2-ene

Ans. *(d)*

While naming the compound, alkene gets priority over functional group (—Br) and numbering starts from alkene side. Hence, IUPAC name: 4-bromo-3-methylpent-2-ene

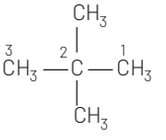


12 The IUPAC name of neopentane is

(a) 2-methylbutane **[AIEEE 2009]**
(b) 2,2-dimethylpropane
(c) 2-methylpropane
(d) 2,2-dimethylbutane

Ans. *(b)*

The neopentane



IUPAC name : 2,2-dimethylpropane

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13 The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is **[AIEEE 2008]**

(a) $-COOH, -SO_3H, -CONH_2, -CHO$

(b) $-SO_3H, -COOH, -CONH_2, -CHO$

(c) $-CHO, -COOH, -SO_3H, -CONH_2$

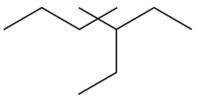
(d) $-CONH_2, -CHO, -SO_3H, -COOH$

Ans. ***(a)***

The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system is

$-COOH > -SO_3H > -COOR > COCl > -CONH_2 > -CN > -CH=O$

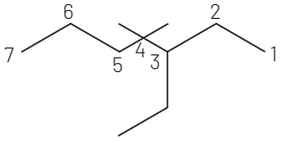
14 The IUPAC name of **[AIEEE 2007]**



is

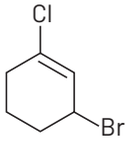
(a) 1, 1-diethyl-2, 2-dimethylpentane
(b) 4, 4-dimethyl-5, 5-diethylpentane
(c) 5, 5-diethyl-4, 4-dimethylpentane
(d) 3-ethyl-4, 4-dimethylheptane

Ans. ***(d)***



3-ethyl-4, 4-dimethylheptane

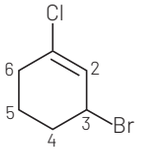
15 The IUPAC name of the compound shown below is **[AIEEE 2006]**



(a) 2-bromo-6-chlorocyclohex-1-ene
(b) 6-bromo-2-chlorocyclohexene
(c) 3-bromo-1-chlorocyclohexene
(d) 1-bromo-3-chlorocyclohexene

Ans. ***(c)***

Unsaturation (double bond) is given priority over halogen. So, the correct IUPAC name is 3-bromo-1-chlorocyclohexene.



16 The number and type of bonds between two carbon atoms in calcium carbide are **[AIEEE 2005]**

(a) two sigma, two pi
(b) two sigma, one pi
(c) one sigma, two pi
(d) one sigma, one pi

Ans. ***(c)***

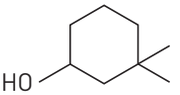
CaC_2 (calcium carbide) is ionic.

$CaC_2 \longrightarrow Ca^{2+} + C_2^{2-}$

$^{-}C \equiv C^{-}$

C_2^{2-} has one σ and two π-bonds.

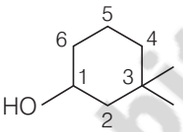
17 The IUPAC name of the compound is



[AIEEE 2004]

(a) 3, 3-dimethyl-1-hydroxy cyclohexane
(b) 1, 1-dimethyl-3-hydroxy cyclohexane
(c) 3, 3-dimethyl-1-cyclohexanol
(d) 1, 1-dimethyl-3-cyclohexanol

Ans. ***(c)***

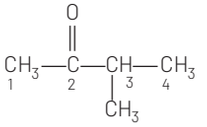


Carbon with $-OH$ group is given C_1, thus it is 3, 3-dimethyl-1-cyclohexanol.

18 The IUPAC name of $CH_3COCH(CH_3)_2$ is **[AIEEE 2003]**

(a) isopropylmethyl ketone
(b) 2-methyl-3-butanone
(c) 4-methylisopropyl ketone
(d) 3-methyl-2-butanone

Ans. ***(d)***



3 -methyl butan-2-one
or 3 -methyl-2-butanone

keto $(-\overset{O}{\overset{\|}{C}}-)$ functional group is given priority.

19 Which of the following compounds has incorrect IUPAC nomenclature? **[AIEEE 2002]**

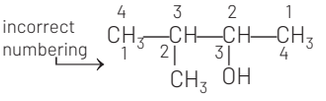
(a) $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$
ethyl butanoate

(b) CH_3CHCH_2CHO (CH_3 branch)
3-methyl butanal

(c) $CH_3CHC(=O)CH_2CH_3$ (CH_3 branch)
2-methyl-3-pentanone

(d) $CH_3CH(H_3C)-CH(OH)-CH_3$
2-methyl-3-butanol

Ans. ***(d)***



Correct name 3-methyl butan-2-ol
or 3-methyl-2-butanol

→ Correct numbering functional group should be given priority

TOPIC 2
Isomerism

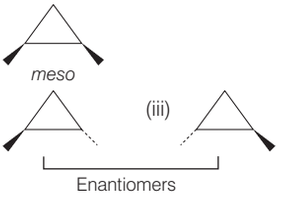
20 The number of stereoisomers possible for 1,2-dimethylcyclopropane is **[2021, 26 Aug Shift-II]**

(a) one (b) four
(c) two (d) three

Ans. ***(d)***

1,2-dimethylcyclopropane is

Hence, stereoisomers are as follows



meso form in optically inactive, whereas enantiomeric pairs are optically active. Therefore, total number of stereo isomers are three (3).

21 Arrange the following conformational isomers of *n*-butane in order of their increasing potential energy **[2021, 31 Aug Shift-II]**

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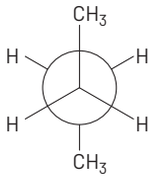
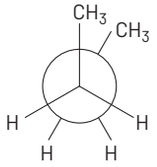
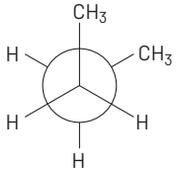
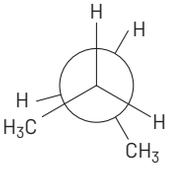
I. 

II. 

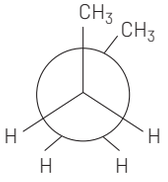
III. 

IV. 

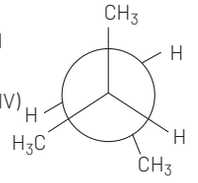
(a) II < III < IV < I (b) I < IV < III < II
(c) II < IV < III < I (d) I < III < IV < II

Ans. ***(d)***

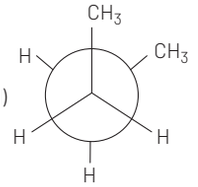
The order of potential energy of above conformations is

(II) 

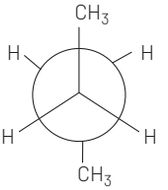
Fully eclipsed

> (IV) 

Partially eclipsed

(III) 

Gauche

> (I) 

Anti

The fully eclipsed form is least stable due to repulsion between bulky (—CH_3) (CH_3) methyl group at front and rear carbon atom.

∴ It has maximum potential energy.

While the repulsion in anti form is minimum.

∴ It has minimum potential energy.

22 The number of acyclic structural isomers (including geometrical isomers) for pentene are ..... .

[2021, 22 July Shift-II]

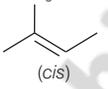
Ans. ***(6)***

(i) $CH_2 = CH - CH_2CH_2CH_3$ (1-pentene)

(ii) $CH_3 - CH = CH - CH_2CH_3$ (2-pentene, it shows geometrical isomerism, i.e. *cis* and *trans*)

(iii) $CH_2 = C(CH_3) - CH_2CH_3$ (2-methyl but-1-ene)

(iv) $(CH_3)_2C = CHCH_3$ (2-methyl but-2-ene)

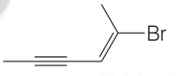


(*cis*)

(v) $(CH_3)_2CH - CH = CH_2$ (3-methyl but-1-ene)

Total number of acyclic structural isomers (including geometrical isomers) for pentene is 6.

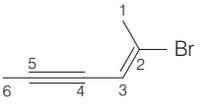
23 Choose the correct name for compound given below



[2021, 31 Aug Shift-I]

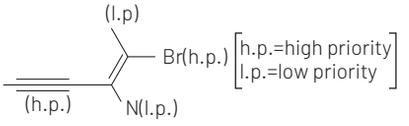
(a) (4E)-5-bromohex-4-en-2-yne
(b) (2E)-2-bromohex-4-yn-2-ene
(c) (2E)-2-bromohex-2-en-4-yne
(d) (4E)-5-bromohex-2-en-4-yne

Ans. ***(c)***



The IUPAC name of above compound is 2-bromohex-2-en-4-yne.

Now, to assign *E/Z* first assign priority to groups along the double bond.



Since, h.p. groups are in opposite direction. So, *E* configuration will be assigned to double bond at second position.

Hence, full IUPAC name of given compound is 2*E*-2-bromohex-2-en-4-yne.

Hence, correct option is (c).

24 Which of the following molecules does not show stereoisomerism ?

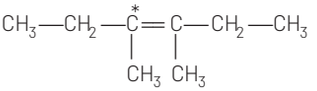
[2021, 22 July Shift-II]

(a) 3, 4 - dimethyl hex-3ene
(b) 3- methyl hex-1-ene
(c) 3 - ethyl hex-3-ene
(d) 4- methyl hex-1-ene

Ans. ***(c)***

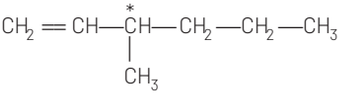
3-ethylhex-3-ene does not show stereoisomerism as it optically inactive due to absence of chiral carbon centre.

(a) 3, 4-dimethylhex-3-ene



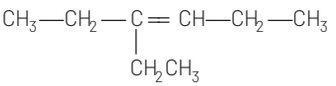
It shows geometrical isomerism i.e *cis/trans*.

(b) 3-methylhex-1-ene



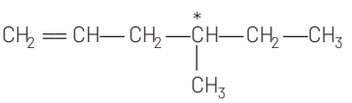
It shows optical isomerism.

(c) 3-ethylhex-3-ene



It cannot show stereoisomerism. i.e. no chiral center.

(d) 4-methylhex-1-ene

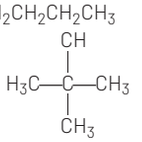


It shows optical isomerism.

Note *C shows chiral carbon.

Hence, 3-ethylhex-3-ene does not show stereo isomerism.

25 Which one of the following pairs of isomers is an example of metamerism ? **[2021, 20 July Shift-II]**

(a) $CH_3CH_2CH_2CH_2CH_3$ and 

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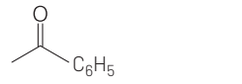
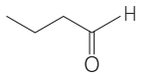
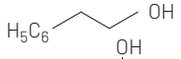
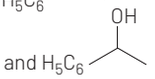
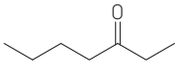
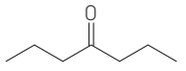
(b) 
and 

(c) 
and 

(d) 
and 

Ans. ***(d)***

Metamers are compounds which have different alkyl groups present along both side of polyvalent functional group.

No polyvalent functional group in option (a).

The two functional groups are different in option (b).

Alcohol is not a polyvalent functional group.

Alkyl groups are different along both sides of polyvalent functional group.

3-heptanone and 4-heptanone

(Metamers)

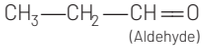
26 Compound with molecular formula C_3H_6O can show

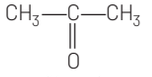
[2021, 18 March Shift-I]

(a) positional isomerism
(b) both positional isomerism and metamerism
(c) metamerism
(d) functional group isomerism

Ans. ***(d)***

Functional isomers are those which have same molecular formula but different functional groups. C_3H_6O molecule can exists as aldehyde as well as ketone as follows

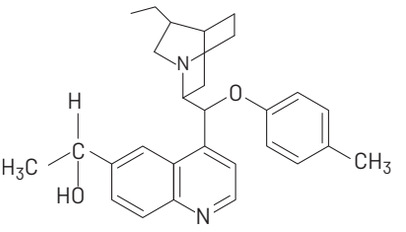

(Aldehyde)

and 
(Ketone)

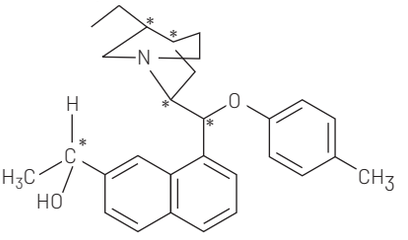
So, they are functional isomers of each other.

27 The number of chiral carbons present in the molecule given below is ..... .

[2020, 2 Sep Shift-I]



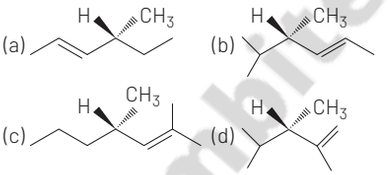
Ans. ***(5)***



The molecule contains five chiral carbon (C*) atoms.

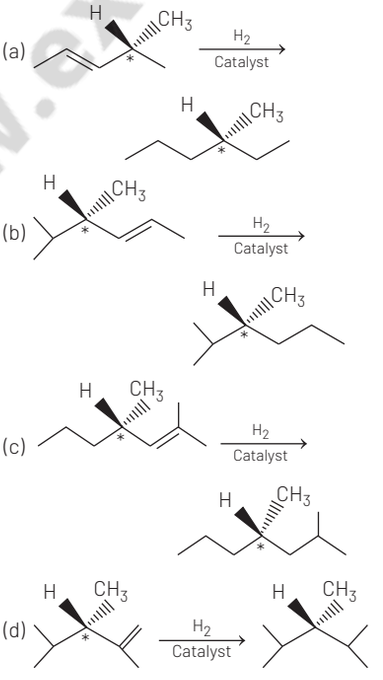
28 Which of the following compounds produces an optically inactive compound on hydrogenation?

[2020, 3 Sep Shift-I]



Ans. ***(d)***

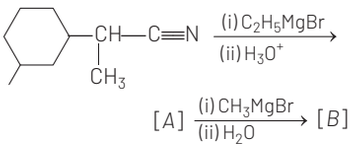
Reaction of all options are as follows :



No change in chirality or optical activity due to hydrogenation of (a), (b) and (c) but in (d) the substrate (alkene) on hydrogenation becomes optically inactive as the product obtained does not have any chiral atom.

29 The number of chiral centres present in [*B*] is ..... .

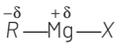
[2020, 4 Sep Shift-I]



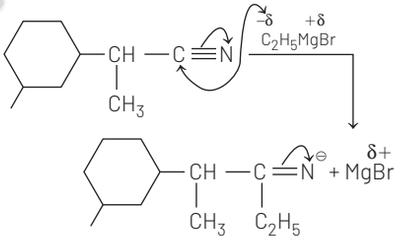
Ans. ***(2)***

Complete reaction is as follows :

(i) C_2H_5MgBr attacks in the form of

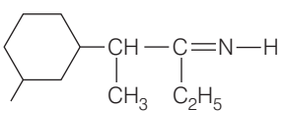


Step I



C_2H_5 contain ($-\delta$) charge attack on carbon.

Step II On hydrolysis following intermediate is formed.

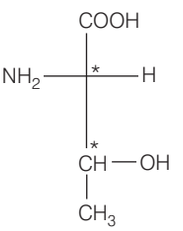


30 The number of chiral centres present in threonine is ..... .

[2020, 4 Sep Shift-II]

Ans. ***(2)***

Structure of threonine is



Threonine have 2 chiral carbon atoms.

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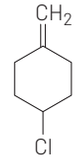
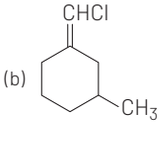
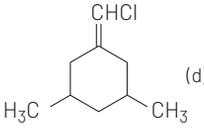
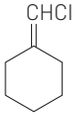
31 Among the following compounds, geometrical isomerism is exhibited by **[2020, 5 Sep Shift-II]**

(a) 

(b) 

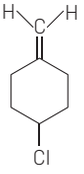
(c) 

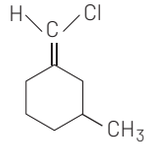
(d) 

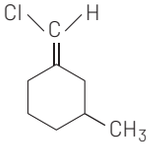
Ans. ***(b)***

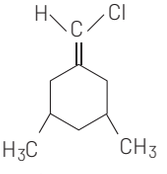
Geometric isomers are molecule that are locked into their saptial positions with respect to one another due to double bond or a ring structure. The presence of restricted rotation is due to double bond or a ring structure.

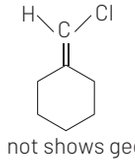
Two different groups must be attached to any two carton atoms of restricted rotation.

(a)  not show geometrical isormerism

(b)  show geometrical (possible *cis* and *trans* isomer)

and 

(c)  not show geometrical isomerism

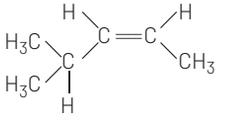
(d)  not shows geometrical isomerism

32 Which of the following compounds shows geometrical isomerism? **[2020, 6 Sep Shift-I]**

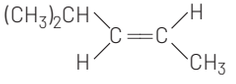
(a) 2-methylpent-2-ene
(b) 4-methylpent-2-ene
(c) 4-methylpent-1-ene
(d) 2-methylpent-1-ene

Ans. ***(b)***

Only 4-methylpent-2-ene shows geometrical isomerism.



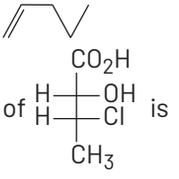
(*cis*-4-methylpent-2-ene)



(*trans*-4-methylpent-2-ene)

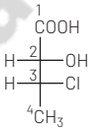
Hence, the correct option is (b).

33 The absolute configuration

 is **[JEE Main 2016]**

(a) (2S, 3R) (b) (2S, 3S)
(c) (2R, 3R) (d) (2R, 3S)

Ans. ***(a)***

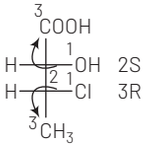


For C-2, order of priority of substituents is OH > CH(Cl)(CH_3)> COOH

For C-3, order of priority of substituents is

Cl > CH(OH)COOH > CH_3

Hence, according to CIP rules,

 2S 3R

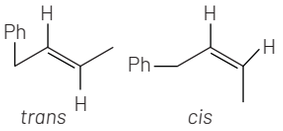
34 Which of the following compound will exhibit geometrical isomerism? **[JEE Main 2015]**

(a) 1-phenyl-2-butene
(b) 3-phenyl-1-butene
(c) 2-phenyl-1-butene
(d) 1, 1-diphenyl-1-propane

Ans. ***(a)***

Alkene in which different groups are attached with the double bonded carbon atoms, exhibit geometrical isomerism.

1-phenyl -2-butene =

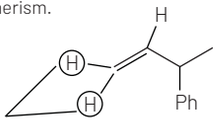


trans *cis*

It will show geometrical isomerism.

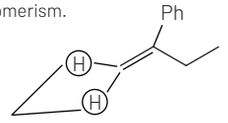
3-phenyl-1-butene

Same group, does not show geometrical isomerism.



2-phenyl-1-butene

Same group, does not show geometrical isomerism.



1,1-diphenyl-1-propane being an alkane (saturated compound) does not show geometrical isomerism.

Time Saving Technique We do not need the check all options, but it should remind that double bonded compounds show geometrical isomerism.

Thus, (d) is eliminated, (i.e. propane).

Now, eliminate the terminal alkene and get the correct response.

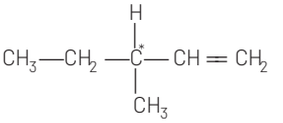
35 Out of the following, the alkene that exhibits optical isomerism is **[AIEEE 2010]**

(a) 3-methyl-2-pentene
(b) 4-methyl-1-pentene
(c) 3-methyl-1-pentene
(d) 2-methyl-2-pentene

Ans. ***(c)***

Optical isomerism is shown by the carbon compounds which possess atleast one chiral carbon.

Thus, 3–methyl–1–pentane possess a chiral carbon, hence it shows optical isomerism.



3-methyl-1-pentene

(It has one chiral centre)

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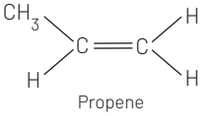
36 The alkene that exhibits geometrical isomerism is **[AIEEE 2009]**

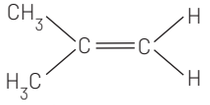
(a) propene
(b) 2-methyl propene
(c) 2-butene
(d) 2-methyl-2-butene

Ans. ***(c)***

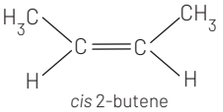
Geometrical isomerism is shown by those alkenes only in which atoms or groups attached to each carbon atom are different. Thus,



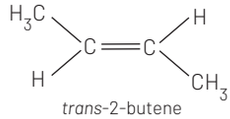
Propene
[three atoms (H) linked to doubly bonded C-atoms are same, thus no geometrical isomerism]



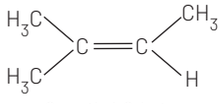
2-methyl propene
(no geometrical isomerism)



cis 2-butene
(methyl group and H-atom linked to doubly bonded C-atom lie on same side, hence *cis* isomer)



trans-2-butene
(methyl groups and H-atom lie on opposite side to one another, hence trans isomer)



2-methyl-2-butene
(no geometrical isomerism)

37 The number of stereoisomers possible for a compound of the molecular formula $CH_3-CH=CH-CH(OH)-Me$ is **[AIEEE 2009]**

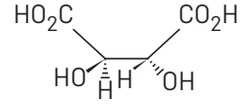
(a) 3 (b) 2
(c) 4 (d) 6

Ans. ***(c)***

There are four stereoisomers.

cis–*R*, *cis*–*S*
trans–*R* *trans*–S

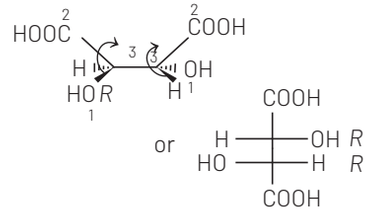
38 The absolute configuration of



[AIEEE 2008]

(a) *S*, *S* (b) *R*, *R* (c) *R*, *S* (d) *S*, *R*

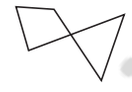
Ans. ***(b)***



39 Which one of the following conformations of cyclohexane is chiral ? **[AIEEE 2007]**

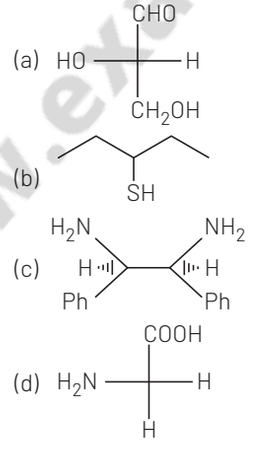
(a) Twist boat (b) Rigid
(c) Chair (d) Boat

Ans. ***(c)***



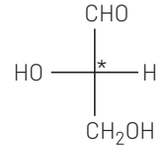
Chair form is unsymmetrical and has absence of any element of symmetry.

40 Which of the following molecules is expected to rotate the plane of polarised light ? **[AIEEE 2007]**

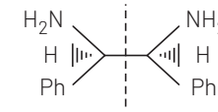


Ans. ***(a)***

The molecule, which is optically active, has chiral centre, is expected to rotate the plane of polarised light.



One chiral centre ⇒ optically active

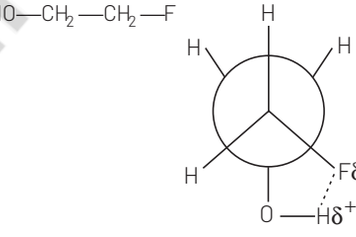


Two chiral centres, but plane of symmetry within molecule ⇒ optically inactive.

41 Increasing order of stability among the three main conformations (*i.e.*, Eclipse, Anti, *Gauche*) of 2-fluoroethanol is **[AIEEE 2006]**

(a) Eclipse, *Gauche*, Anti
(b) *Gauche*, Eclipse, Anti
(c) Eclipse, Anti, *Gauche*
(d) Anti, *Gauche*, Eclipse

Ans. ***(b)***

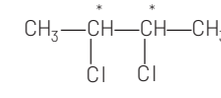


Gauche conformation is comparatively more stable due to hydrogen linkage in between F and H (at O-atom), hence order is eclipse, anti (staggered), *gauche*.

42 Which type of isomerism is shown by 2, 3-dichlorobutane? **[AIEEE 2005]**

(a) Structural (b) Geometric
(c) Optical (d) Diastereo

Ans. ***(c)***



There are two chiral C-atoms (*).

Thus, it shows optical isomerism.

43 For which of the following parameters, the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values? (Assume ideal behaviour) **[AIEEE 2004]**

(a) Heat of vaporisation
(b) Vapour pressure at the same temperature
(c) Boiling points
(d) Gaseous densities at the same temperature and pressure

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Ans. ***(d)***

In CH_3CH_2OH, there is intermolecular H-bonding while it is absent in isomeric ether CH_3OCH_3.

Larger heat is required to vaporise CH_3CH_2OH, as compared to CH_3OCH_3 thus (a) is incorrect.

CH_3CH_2OH, is less volatile than CH_3OCH_3, thus vapour pressures are different, thus (b) is incorrect.

Bp of $CH_3CH_2OH > CH_3OCH_3$, thus (c) is incorrect.

Density $= \frac{\text{mass}}{\text{volume}}$, due to ideal behaviour at a given temperature and pressure, volume and molar mass are same. Hence, they have same vapour density.

44 Which of the following compounds is not chiral ? **[AIEEE 2004]**

(a) 1-chloropentane
(b) 2-chloropentane
(c) 1-chloro-2-methyl pentane
(d) 3-chloro-2-methyl pentane

Ans. ***(a)***

Chiral carbon has all the four different groups attached to it.

(a) $CH_3CH_2CH_2CH_2CH_2Cl$
(no chiral carbon atom)

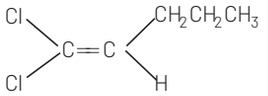
(b) $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_2CH_3$
(one chiral carbon atom)

(c) $CH_3CH_2CH_2\overset{*}{C}HCH_2Cl$
$\quad\quad\quad

50 Geometrical isomerism is not shown by **[AIEEE 2002]**

(a) 1, 1-dichloro-1-pentene
(b) 1, 2-dichloro-1-pentene
(c) 1, 3-dichloro-2-pentene
(d) 1, 4-dichloro-2-pentene

Ans. ***(a)***

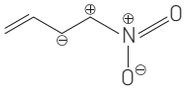


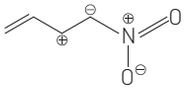
At least two groups or atoms attached to doubly bonded carbon atoms should be different.

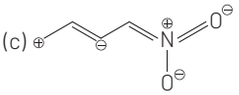
TOPIC 3

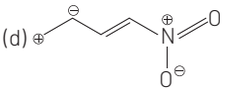
Bond Fission and Electronic Displacement

51 Which one among the following resonating structures is not correct ? **[2021, 25 July Shift-I]**

(a) 

(b) 

(c) 

(d) 

Ans. ***(a)***

Stability of a resonating structure depends on :

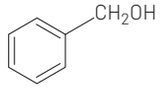
(i) Charge separation between opposite charges should be minimum.

(ii) Charge separation between same charges should be maximum.

Here, two cationic charges in option (a) are very close to each other. So, these charge repel each other. Therefore, structure (a) is unstable.

52 Which of the following compounds does not exhibit resonance ? **[2021, 22 July Shift-II]**

(a) $CH_3CH_2OCH{=}CH_2$

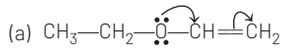
(b) 

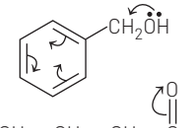
(c) $CH_3CH_2CH_2CONH_2$

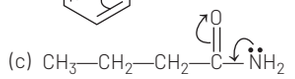
(d) $CH_3CH_2CH{=}CHCH_2NH_2$

Ans. ***(d)***

$CH_3CH_2CH{=}CHCH_2NH_2$ will not show resonance as it does not have conjugated system, whereas; Compounds a, b and c have conjugated system. So, they exhibit resonance.

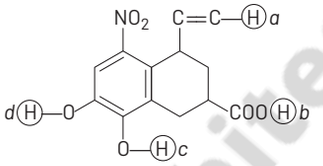
(a) 

(b) 

(c) 

(d) $CH_3CH_2CH{=}CH{-}CH_2{-}NH_2$ (This molecule does not have conjugation).

53 Arrange the following labelled hydrogens in decreasing order of acidity **[2020, 2 Sep Shift-II]**



(a) $b > a > c > d$ (b) $c > b > d > a$
(c) $b > c > d > a$ (d) $c > b > a > d$

Ans. ***(c)***

Carboxylic acids (—COOH) [*b*] are stronger to phenolic —OH groups (*c* and *d*).

Phenolic —OH(*c*) experiences stronger –*R* effect of $-NO_2$ group being placed at para position to (*c*), whereas phenolic —OH(*d*) enjoys comparatively weaker electron withdrawing, –*I* effect of the $-NO_2$ group from *meta*-position.

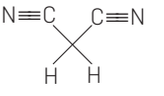
So, acid strength : $c > d$ or $b > c > d$.

The H-atom (*a*) attacked with *sp*-carbon ($s\% = 50$) is also acidic but lesser acidic than H-atoms (*b*, *c* and *d*) who are attacked with more electronegative O-atoms.

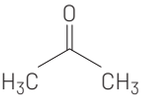
$\therefore$ Electronegativity : O(sp^3) > C(sp)

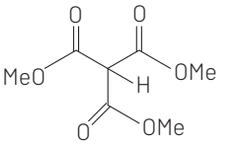
Hence, the order of acidity : $b > c > d > a$.

54 Which one of the following compounds possesses the most acidic hydrogen? **[2020, 3 Sep Shift-I]**

(a) 

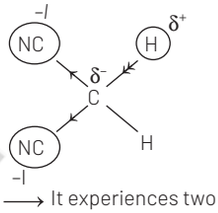
(b) $H_3C{-}C{\equiv}C{-}H$

(c) 

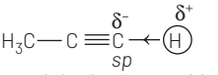
(d) 

Ans. ***(d)***

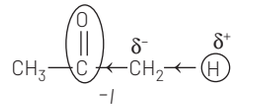
Acidity of H-atom ∝ Attachment with more and stronger electron withdrawing groups.

(a) 

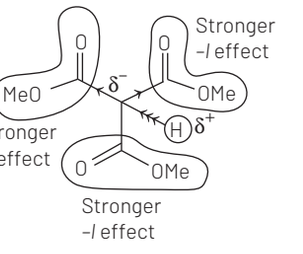
⟶ It experiences two –I effects, so can show acidity

(b) 

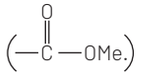
⟶ It is also removable hydrogen

(c) 

⟶ It also shows acidity because of the –I effect

(d) 

⟶ It is most acidic, because the carbon atom bearing this H-atom enjoys three stronger –I effects of enter groups



Compound (d) possess the most acidic hydrogen because of three stronger –*I*-effects.

55 Which of the following has the shortest C—Cl bond? **[2020, 8 Jan Shift-II]**

(a) $Cl{-}CH{=}CH{-}CH_3$
(b) $Cl{-}CH{=}CH{-}NO_2$
(c) $Cl{-}CH{=}CH{-}OCH_3$
(d) $Cl{-}CH{=}CH_2$

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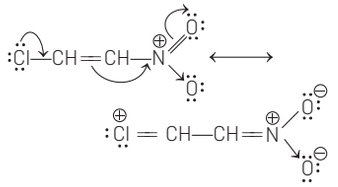
Ans. ***(b)***

Due to $-R$ (or $-M$) effect of 'NO_2', there is stronger double bond character for the 'C—Cl' bond in Cl — CH = CH—NO_2. (option-b)



∴ The bond length is shortest in (b).

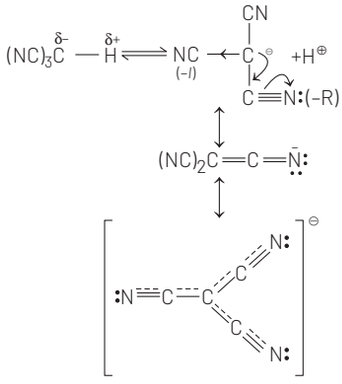
56 Which amongst the following is the strongest acid?

[2019, 9 Jan Shift-I]

(a) $CHBr_3$ (b) CHI_3
(c) $CHCl_3$ (d) $CH(CN)_3$

Ans. ***(d)***

We know, a stronger acid produces its stable or weaker conjugate base. Here, $CH(CN)_3$ produces the most stable conjugate base $(NC)_3C^-$. Stronger $-R$ and $-I$ effects of the CN^- group, make the carbanion (conjugate base) very stable. The resonance hybrid structure of $[(NC)_3C]^-$ is as follows :



Resonance hybrid structure of $[NC)_3C]^-$

57 The correct order for acid strength of compounds
$CH \equiv CH$, $CH_3 — C \equiv CH$ and $CH_2 = CH_2$ is as follows :

(a) $CH_3 — C \equiv CH > CH_2 = CH_2 > HC \equiv CH$
(b) $CH_3 — C \equiv CH > CH \equiv CH > CH_2 = CH_2$
(c) $HC \equiv CH > CH_3 — C \equiv CH > CH_2 = CH_2$
(d) $CH \equiv CH > CH_2 = CH_2 > CH_3 — C \equiv CH$

[2019, 12 Jan Shift-I]

Ans. ***(c)***

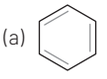
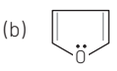
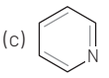
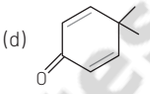
Ethene ($H_2C = CH_2$) is sp^2-hybridised and ethyne ($HC \equiv CH$) is sp-hybridised. In ethyne, the sp-hybridised carbon atom possesses maximum s-character and hence, maximum electronegativity. Due to which, it attracts the shared electron pair of C—H bond to a greater extent and makes the removal of proton easier. Hence, alkyne is much more acidic than alkene.

Presence of electron donating group in alkyne ($H_3C — C \equiv CH$) decreases the acidic strength of compound. Hence, the correct order of acidic strength is:

$HC \equiv CH > H_3C — C = CH > CH_2 = CH_2$

58 Which of the following molecules is least resonance stabilised?

[JEE Main 2017]

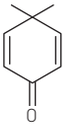
(a) 
(b) 
(c) 
(d) 

Ans. ***(d)***

Aromatic compounds are stable due to resonance while non-aromatics are not. According to Huckel's rule (or $4n + 2$ rule), "For a planar, cyclic compound to be aromatic, its π cloud must contain $(4n + 2)\pi$ electrons, where, n is any whole number." Thus,

$(6\pi e^-$ system) $(4\pi e^- + 2e^-$ system) $(6\pi e^-$ system)

are aromatic and stabilised by resonance. They follow Huckel's rule.



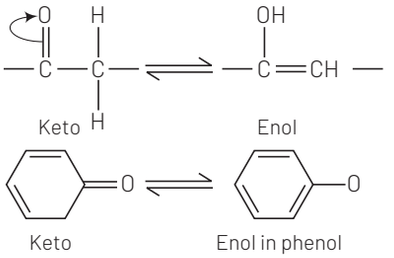
is non-aromatic, hence, least stabilised by resonance.

59 Identify the compound that exhibits tautomerism **[AIEEE 2011]**

(a) 2-butene (b) lactic acid
(c) 2-pentanone (d) phenol

Ans. ***(c), (d)***

Tautomerism is due to spontaneous interconversion of two isomeric forms with different functional groups into one another. The term tautomer means constitutional isomers that undergo such rapid interconversion that can't be independently isolated.



Thus, (c) 2-pentanone and (d) phenol exhibit tautomerism.

60 Consider thiol anion ($RS^{\ominus}$) and alkoxy anion ($RO^{\ominus}$). Which of the following statements is correct? **[AIEEE 2011]**

(a) $RS^{\ominus}$ is less basic and less nucleophilic than $RO^{\ominus}$
(b) $RS^{\ominus}$ is less basic but more nucleophilic than $RO^{\ominus}$
(c) $RS^{\ominus}$ is more basic and more nucleophilic than $RO^{\ominus}$
(d) $RS^{\ominus}$ is more basic but less nucleophilic than $RS^{\ominus}$

Ans. ***(b)***

Nucleophilic strength depends on the electronegativity of the atom. Lower the electronegativity of an atom, larger the nucleophilic strength of an atom and more readily it will donate electrons to the electrophilic (e^- deficient) species.

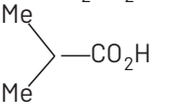
Since, electronegativity decreases down the group, thus nucleophilic strength increases down the group. Hence, RS^- is more nucleophilic than RO^- due to less electronegativity of S than O.

On the other hand, basic strength of an atom depends upon the tendency to accept a proton more readily. Since, O—H bond is longer than S—H bond, thus RO^- has a greater tendency to accept a proton than RS^-. Hence, RO^- is a stronger base than RS^-.

Thus, basic strength of the central atom decreases down the group.

Hence, RS^- is more nucleophilic but less basic than RO^-.

61 The correct order of increasing acid strength of the compounds is **[AIEEE 2006]**

(A) CH_3CO_2H (B) $MeOCH_2CO_2H$
(C) CF_3CO_2H (D) 

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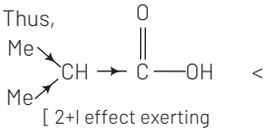
(a) B < D < A < C (b) D < A < C < B
(c) D < A < B < C (d) A < D < C < B

Ans. *(c)*

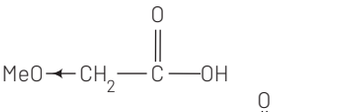
Acidic strength of the compound depends on the ease of release of proton. *I* effect exerting groups [e^- withdrawing] increases the acidic strength while +*I* effect exerting group decreases the strength of an acid.

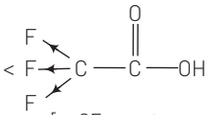
Thus,



[2+I effect exerting groups, increases e^- density on O-atom, thus the release of ease of proton becomes difficult (least acidic)]

[+*I* effect group of $-CH_3$ group]





[$-CF_3$ exerts more –I effect than Meo (most acidic)]

62 Among the following acids which has the lowest pK_a value? **[AIEEE 2005]**

(a) CH_3CH_2COOH
(b) $(CH_3)_2CH$—COOH
(c) HCOOH
(d) CH_3COOH

Ans. *(c)*

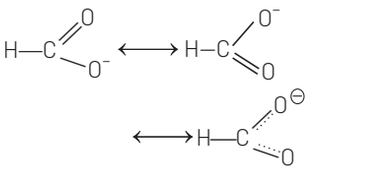
Stronger the acid, lower is their pK_a value. Thus, out of the given acids, strongest acid is HCOOH.

Hence, HCOOH possess lowest pK_a value.

63 In the anion, $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it ? **[AIEEE 2003]**

(a) Electronic orbits of carbon atom are hybridised
(b) The C ═ O bond is weaker than the C—O bond
(c) The anion, $HCOO^-$ has two resonating structures
(d) The anion is obtained by removal of a proton from the acid molecule

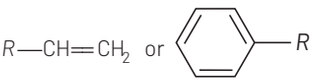
Ans. *(c)*



Resonating (canonical) structures of formate ion

Due to resonance, C—O bonds are found to be of equal length.

64 In the following benzyl/allyl system



(*R* is alkyl group)

decreasing order of inductive effect is **[AIEEE 2002]**

(a) $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2-$
(b) $CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$
(c) $(CH_3)_2CH- > CH_3CH_2- > (CH_3)_3C-$
(d) $(CH_3)_2C- > CH_3CH_2- > (CH_3)_3CH-$

Ans. *(a)*

Both where *R* is attached to vinylic (≈ arylic) system, positive inductive effect occurs in the following order

$-O^- > -COO^- > (CH_3)_3C- >$
$(CH_3)_2CH- > CH_3CH_2- > CH_3-$

TOPIC 4
Reaction Intermediates

65 Given below are two statements.

Statement I Hyperconjugation is a permanent effect.

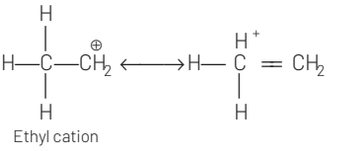
Statement II Hyperconjugation in ethyl cation ($CH_3-\overset{+}{C}H_2$) involves the overlapping of $C_{sp^2}-H_{1s}$ bond with empty 2*p* orbital of other carbon.

Choose the correct option : **[2021, 27 July Shift-II]**

(a) Both statement I and statement II are false.
(b) Statement I is incorrect but statement II is true.
(c) Statement I is true but statement II is false.
(d) Both Statement I and statement II are true.

Ans. *(c)*

Hyperconjugation is a permanent effect.

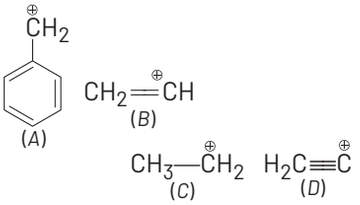


Ethyl cation

Ethyl cation ($CH_3-\overset{+}{C}H_2$) involves overlapping of $C_{sp^3}-H_{1s}$ bond with empty 2*p*-orbital.

∴ Statement I is true and statement II is false.

66

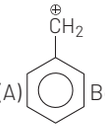


The correct order of stability of given carbocation is **[2021, 27 July Shift-I]**

(a) *A* > *C* > *B* > *D* (b) *D* > *B* > *C* > *A*
(c) *D* > *B* > *A* > *C* (d) *C* > *A* > *D* > *B*

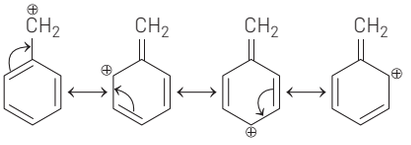
Ans. *(a)*

Correct order of stability of carbocations will be

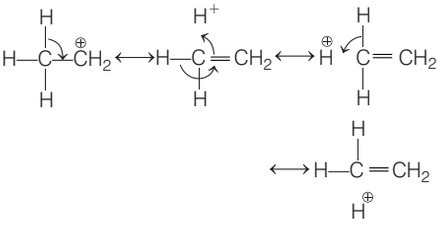


(A) Benzyl carbocation get

stabilise by resonance. It's resonating structures are as follows



(C) $CH_3-\overset{+}{C}H_2$ gets stabilised due to hyperconjugation.



$CH_2=\overset{+}{C}H$(B) and $H_2C\equiv\overset{+}{C}$(D) are not stabilised by resonance or hyperconjugation, thus, they are unstable also positive charge is not stabilised by more electronegative C-atom. Electronegativity of carbon increases with increase in %*s*-character.

For *sp*-hybridised carbon, %*s*-character is 33%.

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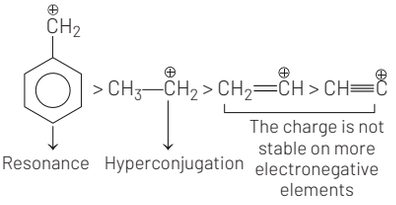
For *sp*-hybridised carbon, %*s*-character is 50%. So, positive charge is less stable on *sp*-hybridised carbon.

So, the correct order of stability of carbocation is

$A > C > B > D.$



67 Which among the following is the strongest acid ?

[2021, 25 July Shift-II]

(a) $CH_3CH_2CH_2CH_3$ (b)

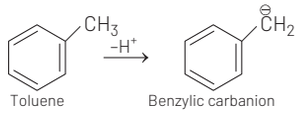
(c) (d)

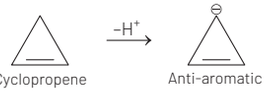
Ans. ***(d)***

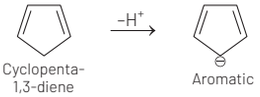
The acid whose conjugate base is most stable will be strongest acid.

(a) $CH_3—CH_2—CH_2—CH_3 \xrightarrow{-H^+}$ Butane

$CH_3—CH_2—CH_2—CH_2^{\ominus}$

(b) 

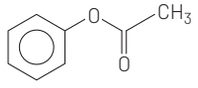
(c) 

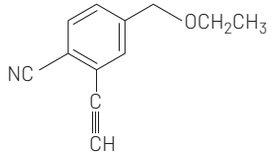
(d) 

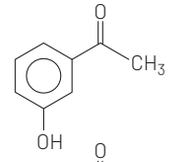
Conjugate base of molecule (d) is most stable as an aromatic compound is formed after donating a proton.

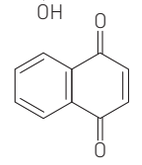
68 Which of the following compounds will provide a tertiary alcohol on reaction with excess of CH_3MgBr followed by hydrolysis ?

[2021, 22 July Shift-II]

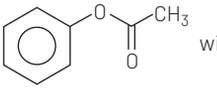
(a) 

(b) 

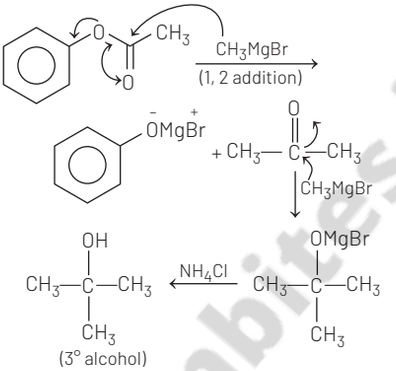
(c) 

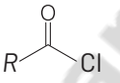
(d) 

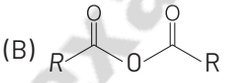
Ans. ***(a)***

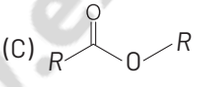
 will provide a tertiary alcohol on reaction with excess of CH_3MgBr followed by hydrolysis.

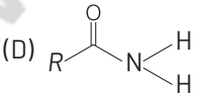
Chemical reaction is as follows;



69 (A) 

(B) 

(C) 

(D) 

The correct order of their reactivity towards hydrolysis at room temperature is

[2021, 20 July Shift-II]

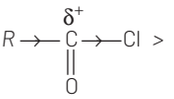
(a) (A) > (B) > (C) > (D)
(b) (D) > (A) > (B) > (C)
(c) (D) > (B) > (A) > (C)
(d) (A) > (C) > (B) > (D)

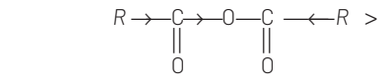
Ans. ***(a)***

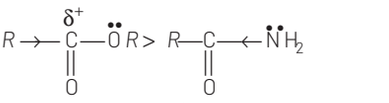
Rate of hydrolysis is directly proportional to positive charged present on carbon of C = O group.

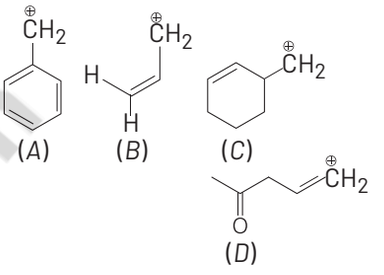
Therefore,

Rate of hydrolysis → Acid chloride > Acid anhydride > Ester > Amide.







70 

Among the given species the resonance stabilised carbocations are

[2021, 20 July Shift-I]

(a) (C) and (D) only
(b) (A), (B) and (D) only
(c) (A) and (B) only
(d) (A), (B) and (C) only

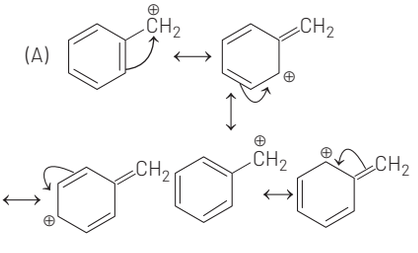
Ans. ***(c)***

Resonance is shown by compound (A) and (B) only, hence they form stable carbocations.

Compound (A) is aromatic and these compounds is stable due to resonance. Whereas in compound (B), double bond and positive charge are in conjugation, hence form stable carbocation due to resonance.

Compound (C) and compound (D) does not shows resonance because double bond and positive charge are not in conjugation.

Only compounds (A) and (B) show resonance as follows

(A) 

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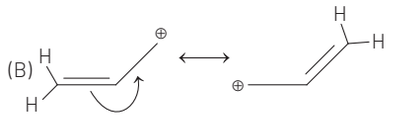
(B) 

71 Given below are two statements.

Statement I C_2H_5OH and AgCN both can generate nucleophile.

Statement II KCN and AgCN both will generate nitrile nucleophile with all reaction conditions.

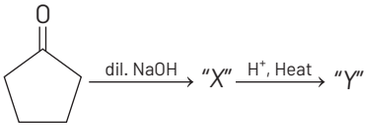
Choose the most appropriate option. **[2021, 18 March Shift-II]**

(a) Statement I is true but statement II is false.
(b) Both statements I and II are true.
(c) Statement I is false but statement II is true.
(d) Both statements I and II are false.

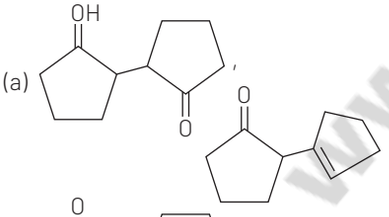
Ans. ***(a)***

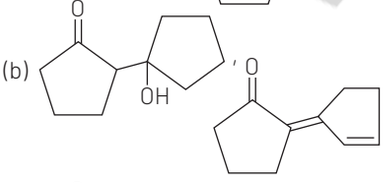
Both C_2H_5OH and AgCN can generate nucleophile. KCN generates nitriles on substitution reactions with haloalkanes, where AgCN generates isonitriles on substitution reactions with haloalkanes. Because KCN is ionic and has 'C' nucleophilic centre whereas AgCN is covalent and has 'N' nucleophilic centre.

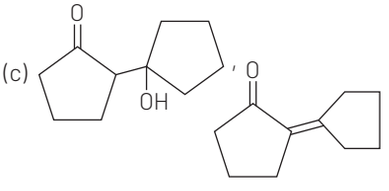
Hence, statement I is true but statement II is false.

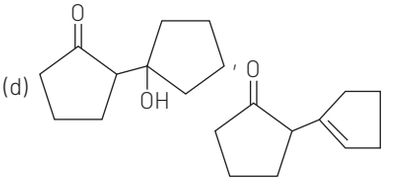
72 

Consider the above reaction, the product '*X*' and '*Y*' respectively are **[2021, 18 March Shift-II]**

(a) 

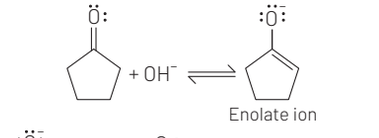
(b) 

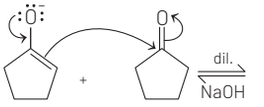
(c) 

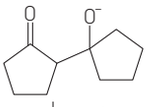
(d) 

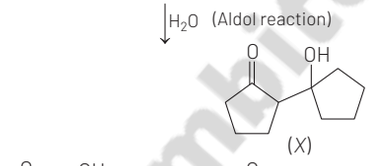
Ans. ***(c)***

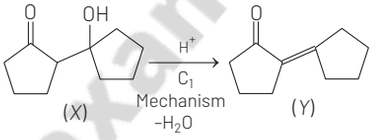
The given reaction is aldol condensation reaction. Here, enolate ion reacts with a carbonyl compound in the presence of dil. NaOH to form a β-hydroxy ketone, followed by dehydration to give a conjugated enone. It take place as follows



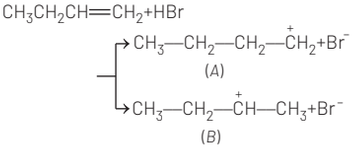








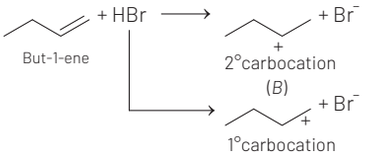
73 Choose the correct statement regarding the formation of carbocations *A* and *B*. **[2021, 17 March Shift-II]**



(a) Carbocation *B* is more stable and formed relatively at faster rate.
(b) Carbocation *A* is more stable and formed relatively at slow rate.
(c) Carbocation *B* is more stable and formed relatively at slow rate.
(d) Carbocation *A* is more stable and formed relatively at faster rate.

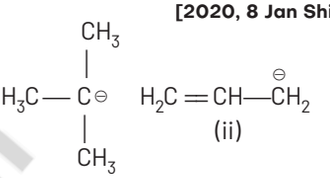
Ans. ***(a)***

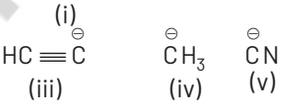
Carbocation *B* is more stable due to more hyperconjugation and formed relatively at faster rate compared to *A*.



Carbocation *B* is more stable as it is secondary carbocation having more number of α-hydrogens, having a greater + *I* effect and formed with faster rate due to low activation energy.

74 The increasing order of basicity for the following intermediates is (from weak to strong) **[2020, 8 Jan Shift-II]**

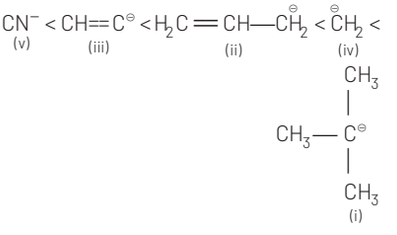




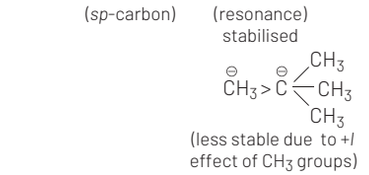
(a) (v) < (iii) < (ii) < (iv) < (i)
(b) (iii) < (i) < (ii) < (iv) < (v)
(c) (v) < (i) < (iv) < (ii) < (iii)
(d) (iii) < (iv) < (ii) < (i) < (v)

Ans. ***(a)***

Basicity order for the following in intermediates is



which is also the opposite of the order of stability of carbanions.



75 The increasing order of nucleophilicity of the following nucleophiles is

(1) $CH_3CO_2^{\ominus}$ (2) H_2O
(3) $CH_3SO_3^{\ominus}$ (4) $\overset{\ominus}{O}H$

[2019, 10 April Shift-II]

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(a) (1) < (4) < (3) < (2)
(b) (2) < (3) < (1) < (4)
(c) (4) < (1) < (3) < (2)
(d) (2) < (3) < (4) < (1)

Ans. ***(b)***

Higher the basicity of a base, stronger will be its nucleophilic power.

Again we know, a weaker acid produces a stronger base (conjugate), i.e. a stronger nucleophile.

$$\text{Acid} \xrightarrow{-H^{\oplus}} \text{Conjugate base}$$

H_3O^+	H_2O
CH_3SO_3H	$CH_3SO_3^{\ominus}$
CH_3CO_2H	$CH_3CO_2^{\ominus}$
H_2O	$^{\ominus}OH$
Acid strength	Base strength ≡ Nucleophilicity

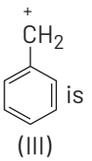
Thus, the correct order of nucleophilicity of given nucleophiles are as follows :

$H_2O(2) < CH_3SO_3^-(3) < CH_3CO_2^-(1) < \bar{O}H(4)$

76 The order of stability of the following carbocations

$CH_2=\overset{+}{C}H-CH_2$;
(I)

$CH_3-CH_2-\overset{+}{C}H_2$;
(II)


(III)

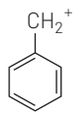
is

[JEE Main 2013]

(a) III > II > I (b) II > III > I
(c) I > II > III (d) III > I > II

Ans. ***(d)***

The order of stability of carbocation will be


Benzyl carbocation (more resonance stabilised)

$> CH_2=CH-\overset{+}{C}H_3 > CH_3-$

Allylcarbocation (resonance stabilised)

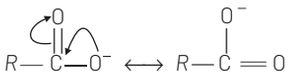
$CH_2-\overset{+}{C}H_2$

Propylcarbocation (stabilised by +*I* effect)

77 The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is **[AIEEE 2010]**

(a) $R\bar{C}OO < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$
(b) $\bar{R} < HC \equiv \bar{C} < R\bar{C}OO < \bar{N}H_2$
(c) $R\bar{C}OO < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$
(d) $R\bar{C}OO < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

Ans. ***(d)***



In carboxylate ion, the negative charge is present on oxygen, a most electronegative element here, thus it is resonance stabilised.

$HC \equiv C^-$: Carbon is *sp* hybridised so its electronegativity is increased higher relative to nitrogen.

$\bar{N}H_2$: Nitrogen is more electronegative than sp^3 hybridised C-atom. From the above discussion, it is clear that the order of the stability of conjugated bases is as

$$R\bar{C}OO^- > HC \equiv C^- > \bar{N}H_2 > R^-$$

and higher is the stability of conjugated bases, lower will be basic character. Hence, the order of basic character is as

$$R\bar{C}OO^- < HC \equiv C^- < \bar{N}H_2 < R^-$$

78 Arrange the carbanions, $(CH_3)_3\bar{C}$, $\bar{C}Cl_3$, $(CH_3)_2\bar{C}H$, $C_6H_5\bar{C}H_2$, in order of their decreasing stability **[AIEEE 2009]**

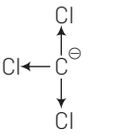
(a) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_2\bar{C} > (CH_3)_2\bar{C}H$
(b) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$
(c) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$
(d) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > \bar{C}H_2 > \bar{C}Cl_3$

Ans. ***(c)***

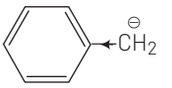
$-I$ effect [e^- withdrawing] exerting groups stablises carbanion by the dispersal of their –ve charge while $+I$ effect exerting [e^- releasing] groups destablises the carbanion by increasing electron density on them.

On the other hand, resonance stablised carbanion are stable due to the involvement of their lone pair of electron with the delocalisation of π–electrons of attached phenyl group.

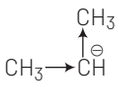
Thus,


(3-*I* effect exerting group of Cl)

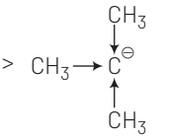
$>$


(–*I* effect of phenyl group as well as delocalisation of electrons)

$>$


(+ *I* effect of 2-CH_3 group)

$>$

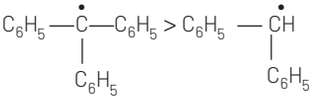

(+ *I* effect of 3 - CH_3 groups)

79 The increasing order of stability of the following free radicals is **[AIEEE 2006]**

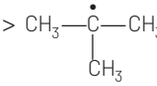
(a) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$
(b) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
(c) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
(d) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

Ans. ***(a)***

Free radicals stability


(highly stable by delocalisation of 3 phenyl groups)

$>$



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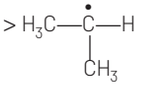
(9-hyperconjugative hydrogens and + I effect of 3 alkyl group)

80 Due to the presence of an unpaired electron, free radicals are **[AIEEE 2005]**

(a) cations
(b) anions
(c) chemically inactive
(d) chemically reactive

Ans. ***(d)***

Free radicals have unpaired electrons, so are neutral and reactive.

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$$

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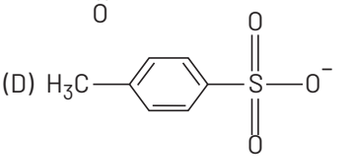
81 The decreasing order of nucleophilicity among the nucleophiles **[AIEEE 2005]**

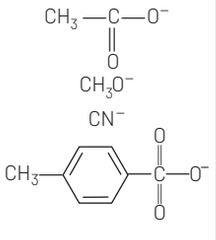
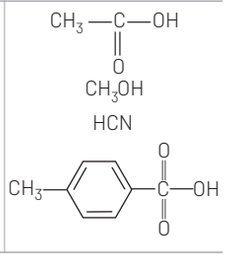
(A) $CH_3\overset{\overset{O}{\|}}{C}-O^-$ (B) CH_3O^- (C) CN^-

(D) 

(a) (C), (B), (A), (D) (b) (B), (C), (A), (D)
(c) (D), (C), (B), (A) (d) (A), (B), (C), (D)

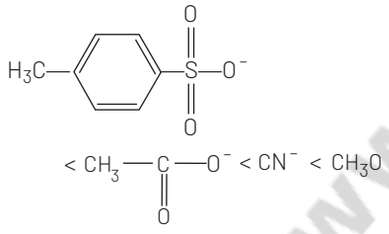
Ans. ***(b)***

Weaker the acid, more stable is their conjugate base and greater is their nucleophilicity. Thus, nucleophilicity order of the conjugate bases is opposite to their acidic strength.

Conjugate bases	Acids
	

Since, alcohols and cyanides are weaker acid than sulphonic and carboxylic acids. Thus, the order of acidic strength of the given species are

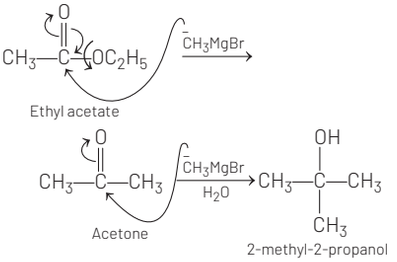
Hence, the decreasing order of nucleophicity of the given nucleophiles is as follows

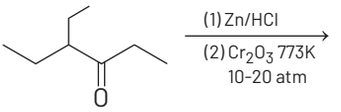


82 To synthesis 1.0 mole of 2-methylpropan -2-ol from ethylethanoate ..... equivalents of CH_3MgBr reagent will be required. (Integer value) **[2021, 20 July Shift-I]**

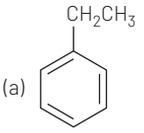
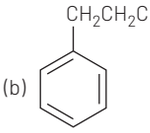
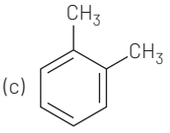
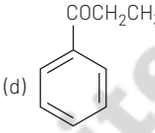
Ans. ***(2)***

2 moles of CH_3MgBr reagent will be used. Chemical reaction is as follows



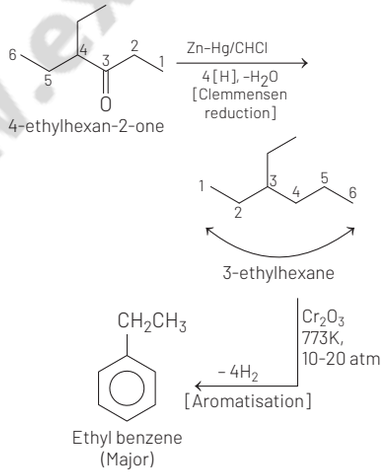
83 

considering the above reaction, the major product among the following is **[2021, 26 Feb Shift-II]**

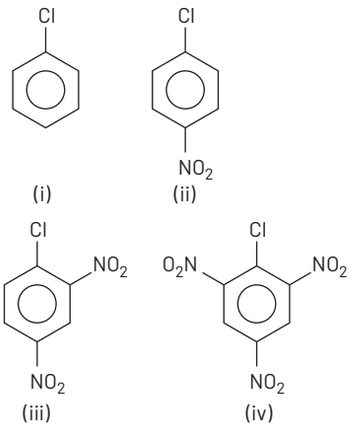
(a) 
(b) 
(c) 
(d) 

Ans. ***(a)***

In this reaction, an open chain ketone (4-ethyl hexan -2- one) undergoes Clemmensen reduction first to give 3-ethylhexane which on aromatisation produces an aromatic hydrocarbon, ethyl benzene [option -(a)] as the major product.



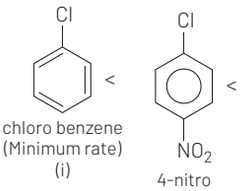
84 The correct order of the following compounds showing increasing tendency towards nucleophilic substitution reaction is **[2021, 24 Feb Shift-II]**

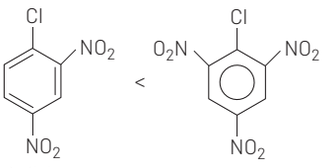


(a) (iv) < (iii) < (ii) < (i)
(b) (iv) < (i) < (ii) < (iii)
(c) (iv) < (i) < (iii) < (ii)
(d) (i) < (ii) < (iii) < (iv)

Ans. ***(d)***

Rate of nucleophilic substitution in aromatic halide are as follows

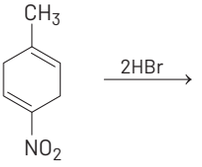




Greater the number of nitro (—NO_2) group in chlorobenzene, greater the rate of nucleophilic substitution reaction in aromatic halides.

When a nitro group is present at *ortho* and *para* position, it can withdraw electrons from the benzene ring. This facilitates, the attack of nucleophiles on haloarenes.

85 The major product of the following reaction is



[2020, 6 Sep Shift-I]

TOPIC 5
Types of Organic Reactions

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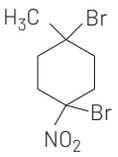
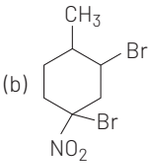
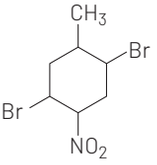
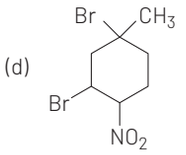
(a) 

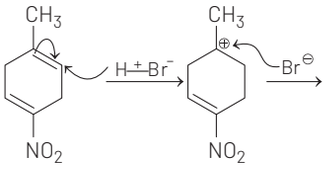
(b) 

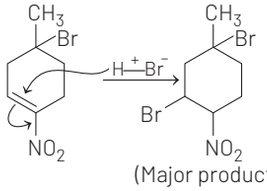
(c) 

(d) 

Ans. ***(d)***

Addition of HBr to unsymmetrical alkene take place according to Markownikoff's rule.





(Major product)

Hence, the correct option is (d).

86 Consider the following reactions:

$(A)\ (C_7H_{14}) \xrightarrow{\text{Ozonolysis}} (B) + (C)$

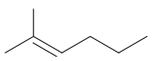
'B' $\xrightarrow[\Delta]{(I_2 + NaOH)}$ yellow ppt.

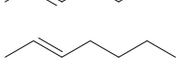
'B' $\xrightarrow[\Delta]{Ag_2O}$ Silver mirror

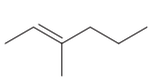
(C) $\xrightarrow[\Delta]{(I_2 + NaOH)}$ no yellow ppt.

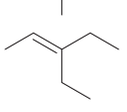
(C) $\xrightarrow[\Delta]{LiAlH_4}$ (D) $\xrightarrow[\text{and conc. HCl}]{\text{Anhydrous } ZnCl_2}$ Gives white turbidity within 5 minutes

(A) is **[2020, 6 Sep Shift-I]**

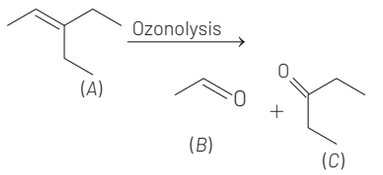
(a) 

(b) 

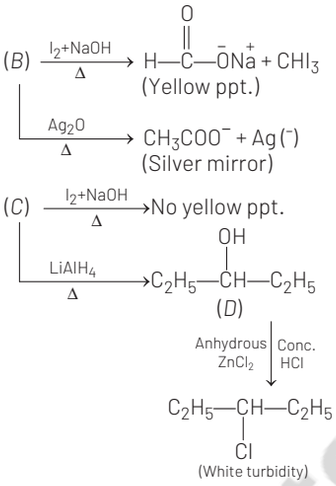
(c) 

(d) 

Ans. ***(d)***



Alkene (A) undergoes ozonolysis and gives an aldehyde and ketone.

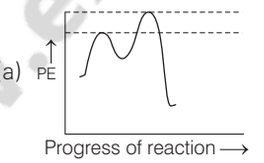


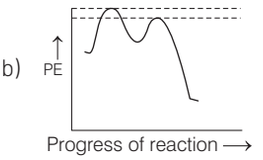
Methyl ketones react with I_2 + NaOH, so option (a) and (c) are incorrect, while option (b) only gives aldehydes, thus (b) also incorrect.

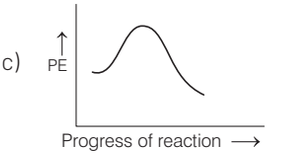
Hence, the correct option is (d).

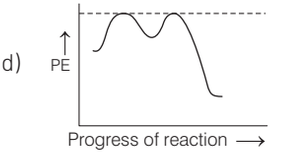
87 Which of the following potential energy (PE) diagrams represents the S_N1 reaction?

[2019, 9 April Shift-II]

(a) 

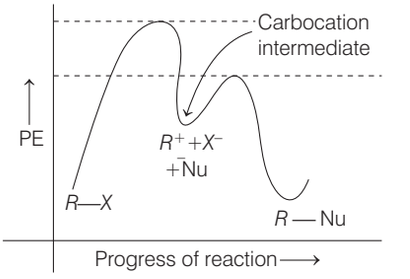
(b) 

(c) 

(d) 

Ans. ***(b)***

The potential energy (PE) diagram for S_N1 reaction is



S_N1 reaction has two steps. In the first step, the carbon halogen bond breaks heterolytically, with the halogen retaining the previously shared pair of electron. In the second step, the nucleophile reacts rapidly with the carbocation formed in the first step.

In the above graph, the alkyl halide is the only species that participates in the rate limiting step. Here, the rate of reaction depends on the concentration of the alkyl halide and does not depend on the concentration of nucleophile.

88 Which of the following is the correct order of decreasing S_N2 reactivity? (X = a halogen)

[AIEEE 2007]

(a) $RCH_2X > R_3CX > R_2CHX$

(b) $RCH_2X > R_2CHX > R_3CX$

(c) $R_3CX > R_2CHX > RCH_2X$

(d) $R_2CH_2X > R_3CX > RCH_2X$

Ans. ***(b)***

S_N2 reactions are greatly controlled by steric factor.

$\underset{1^\circ}{R{-}CH_2{-}X}, \underset{2^\circ}{R_2CH{-}X}, \underset{3^\circ}{R_3C{-}X}$

S_N2 reactivity decreases as bulkyness of alkyl group increases.

89 Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of

[AIEEE 2005]

(a) steric hindrance

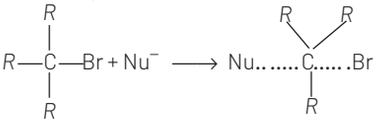
(b) inductive effect

(c) instability

(d) insolubility

Ans. ***(a)***

In S_N2 reaction, attack of nucleophile and breaking of C—Br bond takes place in one step.



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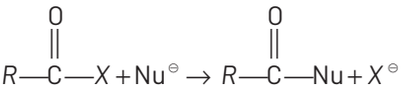
Since, tertiary carbon is sterically hindered, thus the attack of nucleophile becomes difficult. Hence, tertiary alkyl halides undergo S_N2 reaction very rarely.

90 The reaction

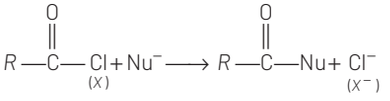


is fastest when *X* is **[AIEEE 2005, 2004]**

(a) OCO*R* (b) OC_2H_5
(c) NH_2 (d) Cl

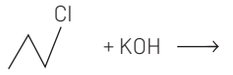
Ans. ***(d)***

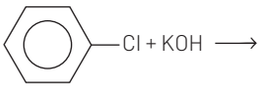
Poor the nucleophile, better is the leaving group ability. Among the given species, Cl^- is a poor nucleophile, thus it will act as a better leaving group. Thus, *X* will be Cl and hence, the given reaction will be fast in the presence of Cl.

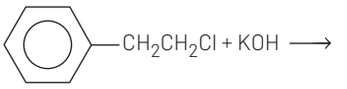


91 S_N1 reaction is feasible in **[AIEEE 2002]**

(a)

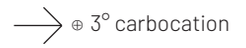
(b) 

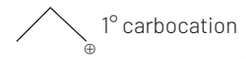
(c) 

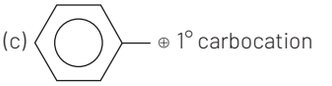
(d) 

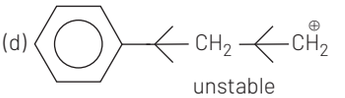
Ans. ***(a)***

S_N1 (unimolecular nucleophilic substitution) reaction is favoured with stability of carbocation.

(a)  ⊕ 3° carbocation

(b)  1° carbocation

(c)  ⊕ 1° carbocation

(d) 

unstable 1° carbocation (due to the presence of - *I* effect exerting phenyl group)

92 Following reaction, $(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$ is an example of **[AIEEE 2002]**

(a) elimination reaction
(b) free radical substitution
(c) nucleophilic substitution
(d) electrophilic substitution

Ans. ***(c)***

$(CH_3)_3C—Br + H_2O \longrightarrow (CH_3)_3C—OH + HBr$

Here, Br is substituted by $—OH^-$ (nucleophile)

$\rightarrow S_N1$ reaction (unimolecular substitution reaction)

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23

Hydrocarbons

TOPIC 1
Alkanes

01 Experimentally reducing a functional group cannot be done by which one of the following reagents ? **[2021, 1 Sep Shift-II]**

(a) Pt-C/H_2 (b) Na / H_2

(c) Pd-C/H_2 (d) Zn / H_2O

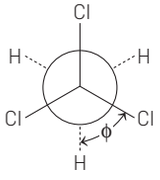
Ans. ***(b)***

A functional group cannot be reduced by Na/H_2 as it is not a reducing agent.

02 The dihedral angle in staggered form of Newman projection of 1, 1, 1-trichloro ethane is ..... degree. (Round off to the nearest integer) **[2021, 27 July Shift-II]**

Ans. ***(60)***

Newman staggered form of 1,1,1-trichloro ethane (CCl_3—CH_3).



Dihedral angles (ϕ) =60°

03 Given below are two statements.

Statement-I 2-methylbutane on oxidation with $KMnO_4$ gives 2-methylbutan-2-ol.

Statement-II *n*-alkanes can be easily oxidised to corresponding alcohols with $KMnO_4$.

Choose the correct option. **[2021, 17 March Shift-II]**

(a) Both statements I and II are correct.

(b) Both statements I and II are incorrect.

(c) Statement I is correct but statement II is incorrect.

(d) Statement I is incorrect but statement II is correct.

Ans. ***(c)***

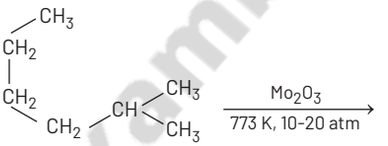
Statement I is correct, whereas statement II is incorrect. Corrected statement is as follows:

Tertiary alkanes can be oxidised to alcohol by treating with $KMnO_4$.

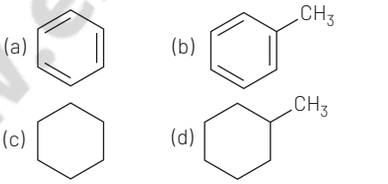
n-alkane are very less reactive and have no reaction with $KMnO_4$.

n-alkanes $\xrightarrow{KMnO_4}$ No reaction

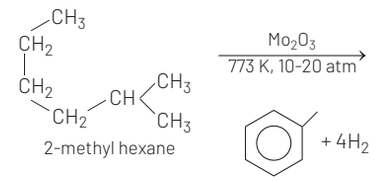
04 Identify *A* in the given chemical reaction. **[2021, 25 Feb Shift-I]**



'A'
(Major product)



Ans. ***(b)***



2-methyl hexane

Toluene

Oxides of molybdenum, vanadium and chromium, i.e. Mo_2O_3, V_2O_5 and Cr_2O_3 work as catalyst. When they are operated under certain temperature and pressure with *n*-heptane then they form toluene which is aromatic compound. Mo_2O_3 behave as aromatising agent.

05 Which of these factors does not govern the stability of a conformation in acyclic compounds? **[2019, 10 April, Shift-II]**

(a) Electrostatic forces of interaction

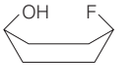
(b) Torsional strain

(c) Angle strain

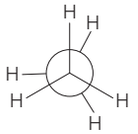
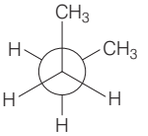
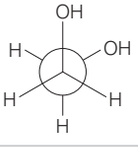
(d) Steric interactions

Ans. ***(c)***

The four types of strains *viz* (a) electrostatic force of attraction, (b) torsional strain, (c) angle strain, (d) steric stain, are responsible for the stability or energy barriers of conformers. In cyclic compounds, all types of strains may be present.

Compound	Type of strains/forces
	a + *c*
	a + *b* + *c*
	*a* + *b* + *c* + *d*

In a cyclic or open-chain compounds, angle strain (c) is absent. e.g.

Compound	Types of strains/forces
	*a*
	*a* + *b*
	*a* + *b* + *d*

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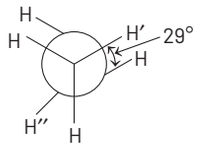
06 In the following skew conformation of ethane, H′—C—C—H′′ dihedral angle is



[2019, 12 April Shift-II]

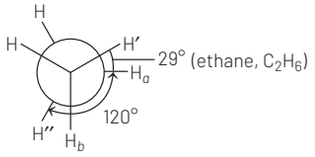
(a) 58° (b) 149°
(c) 151° (d) 120°

Ans. ***(b)***

A dihedral angle is the angle between two C—H bonds projected on a plane orthogonal to the C—C bond. In the given skew conformation, having Newman's projection the dihedral angle is

H′—C—C—H′′
$=(H'—C—C—H_a)+(H_a—C—C—H'')$

$=29°+120°=149°$



07 Alkyl halides react with dialkyl copper reagents to give **[AIEEE 2005]**

(a) alkenyl halides
(b) alkanes
(c) alkyl copper halides
(d) alkenes

Ans. ***(b)***

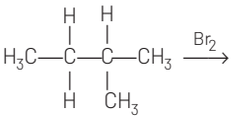
$R_2CuLi + R'X \longrightarrow R—R' + R—Cu + LiX$

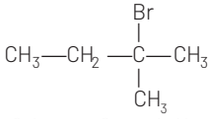
(dialkyl copper lithium)

08 2-methyl butane on reacting with bromine in the presence of sunlight gives mainly **[AIEEE 2005]**

(a) 1-bromo-3-methylbutane
(b) 2-bromo-3-methylbutane
(c) 2-bromo-2-methylbutane
(d) 1-bromo-2-methylbutane

Ans. ***(c)***





2-bromo- 2- methyl butane

09 Of the five isomeric hexanes , the isomer which can give two monochlorinated compounds, is **[AIEEE 2005]**

(a) 2-methylpentane
(b) 2,2-dimethylbutane
(c) 2,3-dimethylbutane
(d) *n*-hexane

Ans. ***(c)***

(a) 2-methylpentane $\xrightarrow{Cl_2}$ five types of monochlorinated compounds

(b) 2, 2-dimethylbutane $\xrightarrow{Cl_2}$ three types

(c) 2, 3-dimethylbutane $\xrightarrow{Cl_2}$ two types

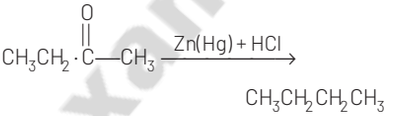
(d) *n*-hexane $\xrightarrow{Cl_2}$ three types

10 Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon? **[AIEEE 2004]**

(a) Ethyl acetate (b) Acetic acid
(c) Acetamide (d) Butan-2-one

Ans. ***(d)***

Carbonyl compounds are reduced to corresponding alkanes with (Zn + conc. HCl). It is called Clemmensen reduction.



11 Which one of the following has the minimum boiling point? **[AIEEE 2004]**

(a) *n*-butane (b) 1-butyne
(c) 1-butene (d) Isobutene

Ans. ***(d)***

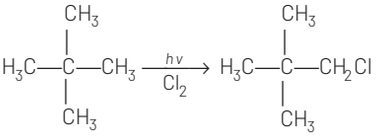
Isobutene $(H_3C)_2C=CH_2$ has minimum force of attraction (due to steric hindrance). Thus, minimum boiling point.

12 On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be **[AIEEE 2003]**

(a) propane
(b) pentane
(c) isopentane
(d) neopentane

Ans. ***(d)***

In neopentane, all H are equivalents.



13 Butene-1 may be converted to butane by reaction with **[AIEEE 2003]**

(a) Zn-HCl (b) Sn-HCl
(c) Zn-Hg (d) Pd/H_2

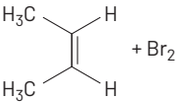
Ans. ***(d)***

$\underset{\text{Butene-1}}{CH_2=CHCH_2CH_3} \xrightarrow[\Delta\text{, pressure}]{Pd/H_2} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$

Other reagents are successful with polar double bonds.

TOPIC 2
Alkenes

14



$\xrightarrow{CCl_4}$ Product (*P*)

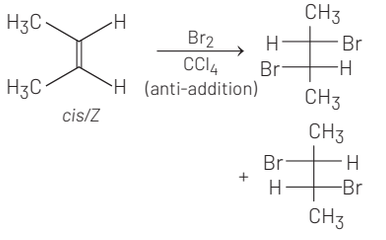
Consider the above chemical reaction. The total number of stereoisomers possible for product *P* is .....

[2021, 25 July Shift-II]

Ans. ***(2)***

Br_2 / CCl_4 gives anti-addition of bromine with alkene but product formed in the reaction depends upon the stereo of alkene (*E* or *Z* alkene).

Here, *cis* alkene /Z-alkene is given, so we get racemic mixture of two isomers.



The total number of products possible = 2

Mechanism First *cis*-alkene reacts with Br_2 to form bromonium ion and then ring opening takes place by nucleophile Br^- to form two racemic products.

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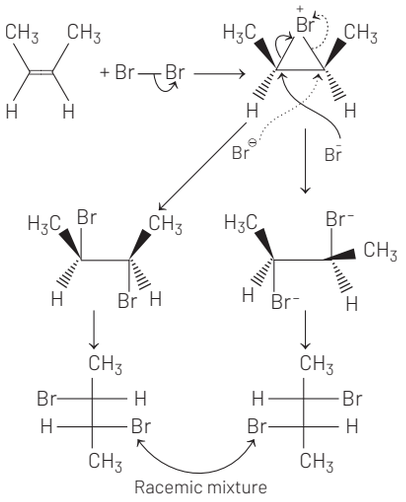
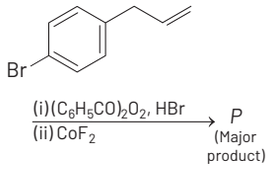
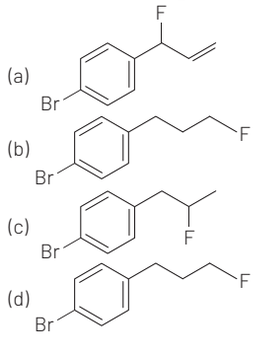


15

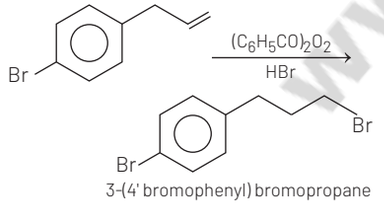


Major product *P* of above reaction is **[2021, 20 July Shift-II]**



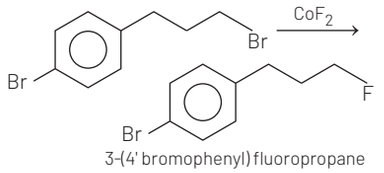
Ans. ***(d)***

Addition of HBr in presence of peroxide follows anti-Markownikoff rule. i.e. hydrogen atoms are attached to carbon atom with least hydrogen substituents.



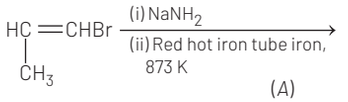
3-(4' bromophenyl) bromopropane

On reaction with CoF_2, bromine is replaced by fluorine in haloalkanes. This reaction is known as Swarts reaction.

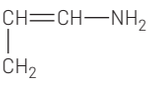


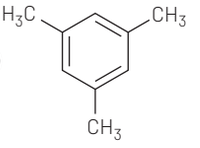
3-(4' bromophenyl) fluoropropane

16 For the given reaction **[2021, 26 Feb Shift-I]**



(*A*)
Major product

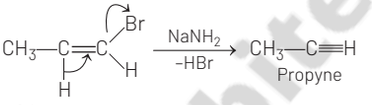
(a) $CH_3CH_2CH_2NH_2$ (b) 

(c) (d) 

Ans. ***(d)***

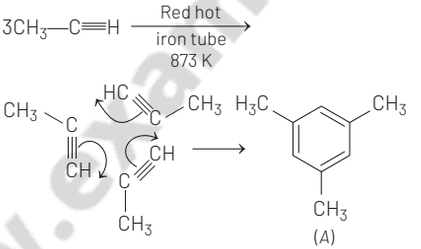
When 1-bromo-prop-1-ene reacts with $NaNH_2$ (a strong base), β-elimination or dehydrobromination, (–HBr) takes place to give propyne in next step. When propyne is passed through red hot iron tube, cyclic trimerisation (aromatisation also) occurs to produce mesitylene (*A*) as major product.

Step I



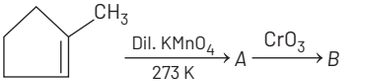
1-bromo-propene

Step II

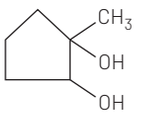
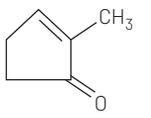


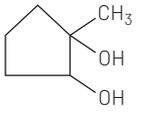
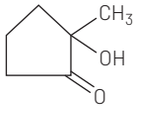
(*A*)
(Major)
Mesitylene or
1, 3, 5-trimethyl benzene

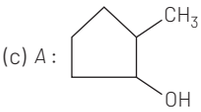
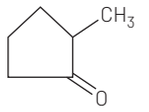
17 Identify products *A* and *B*.

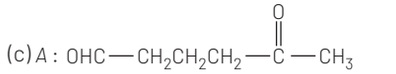


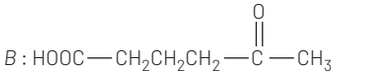
[2021, 24 Feb Shift-I]

(a) *A* :  *B* : 

(b) *A* :  B : 

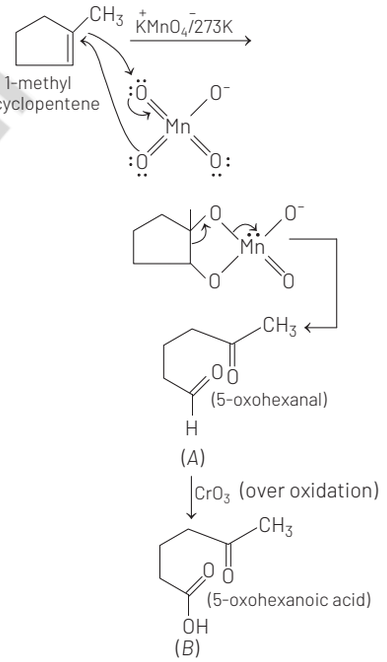
(c) *A* :  *B* : 

(c) *A* : 

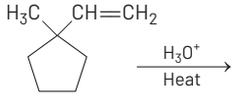
B : 

Ans. ***(d)***

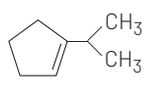
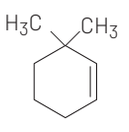
In first step, $KMnO_4$ (dil.) help to break alkene in ketone and aldehyde and in second step, CrO_3 is used for selective over oxidation of aldehyde only. CrO_3 will form aldehyde to acid in product (*B*).

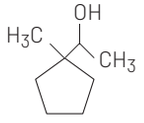
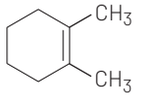


18 The major product in the following reaction is



[2020, 2 Sep Shift-I]

(a)  (b) 

(c)  (d) 

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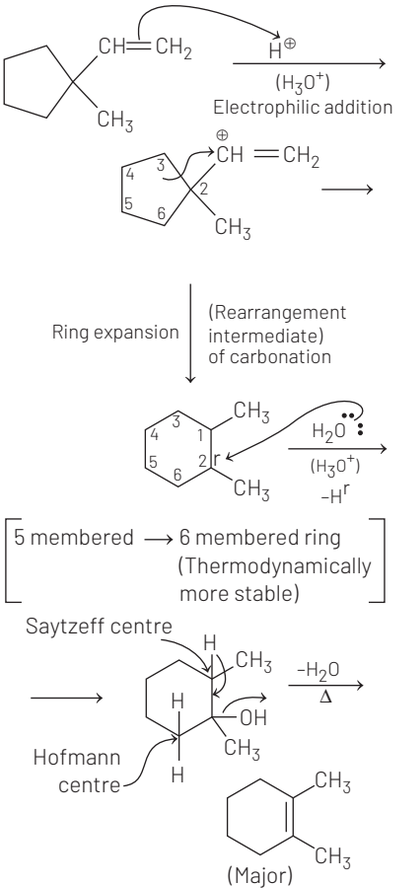
Ans. ***(d)***

Complete mechanism is as follows:



The major product obtained in the given reaction is 1, 2-dimethyl cyclohexene.

19 The major product obtained from E_2-elimination of 3-bromo-2-fluoropentane is

[2020, 2 Sep Shift-II]

(a) $CH_3CH_2-\underset{Br}{CH}-CH_2=CH_2$

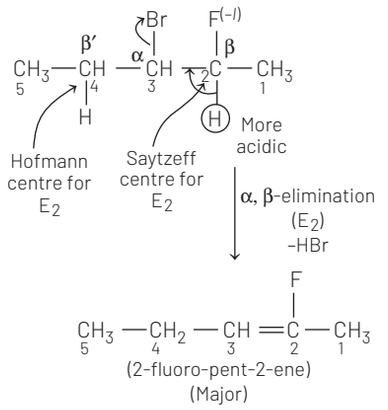
(b) $CH_3CH_2CH=\underset{CH_3}{C}-F$

(c) $CH_3-CH=CH-\underset{Br}{\underset{|}{C}}H-\underset{F}{\underset{|}{C}}H-CH_3$

(d) $CH_3-CH_2-\underset{Br}{\underset{|}{C}}=CH-CH_3$

Ans. ***(b)***

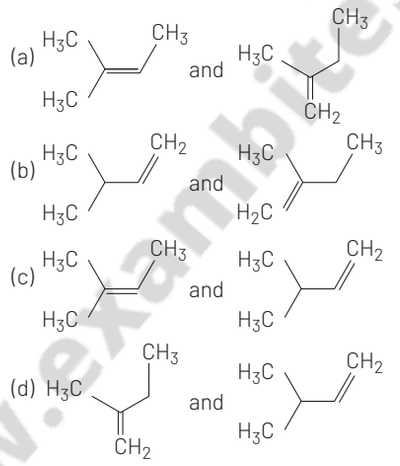
Br atom is larger than F atom. So, C—Br is weaker than C—F bond. In elimination (E_2), C—Br bond will be cleared.



–*I*-effect of F atom makes the β-hydrogen more acidic for its elimination by a strong base used in E_2.

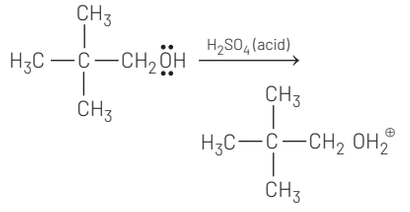
20 When neopentyl alcohol is heated with an acid, it slowly converted into an 85 : 15 mixture of alkenes *A* and *B*, respectively. What are these alkenes?

[2020, 4 Sep Shift-I]



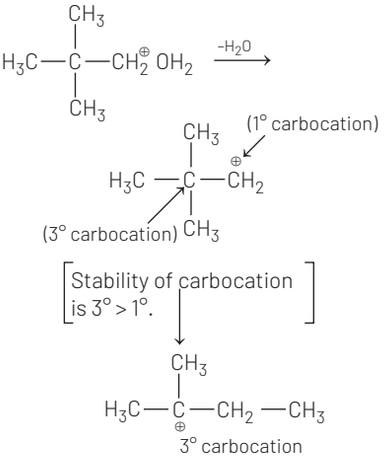
Ans. ***(a)***

Reaction is as follows :



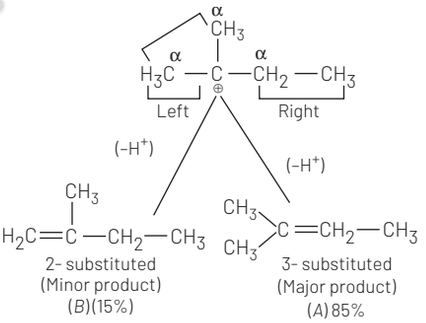
H_2SO_4 is sulphuric acid, that contain $H^{\oplus}$ and alcohol of contain lone pair.

Lone pair of oxygen accept $H^{\oplus}$ ion and form $\overset{\oplus}{O}H_2$ but oxygen is electronegative element and here O contain positive charge means it is unstable. Then H_2O will remove from here.



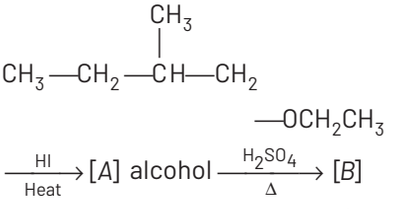
On heating 3° carbocation, 2 possible products are possible.

These are as follows :



So, correct option is (a).

21 The major product [*B*] in the following reactions is



[2020, 4 Sep Shift-II]

(a) $CH_3-CH=\underset{CH_3}{C}-CH_3$

(b) $CH_2=CH_2$

(c) $CH_3-CH_2-\underset{CH_3}{C}=CH_2$

(d) $CH_3-CH_2-CH=CH-CH_3$

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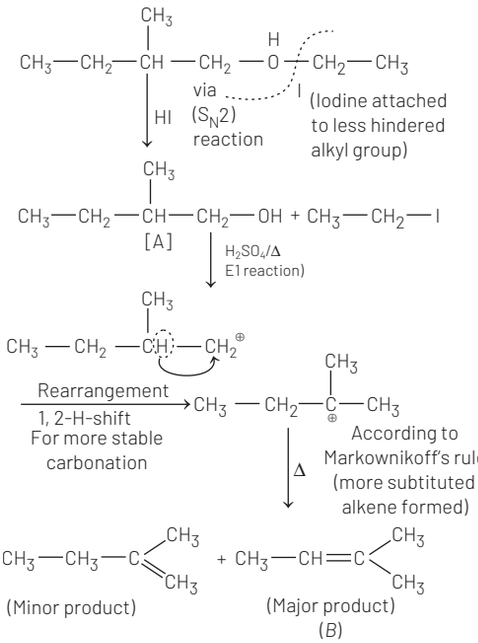
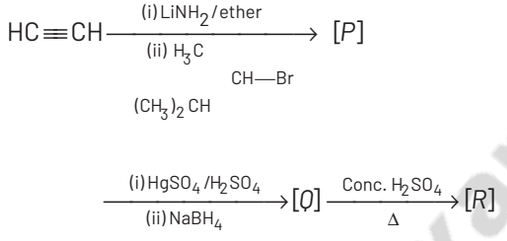
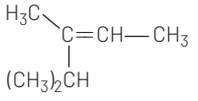
Ans. ***(a)***

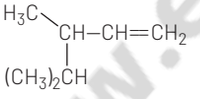


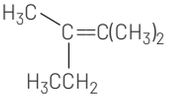
22 The major product [*R*] in the following sequence of reactions is

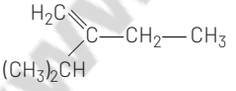


[2020, 4 Sep Shift-II]

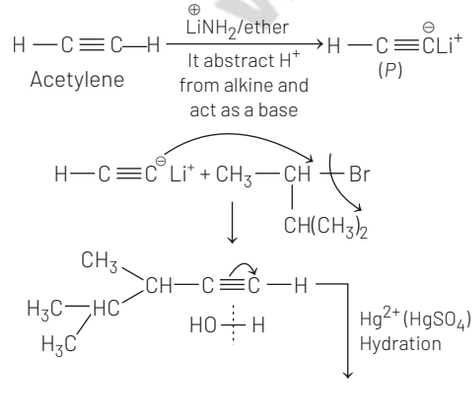
(a) 

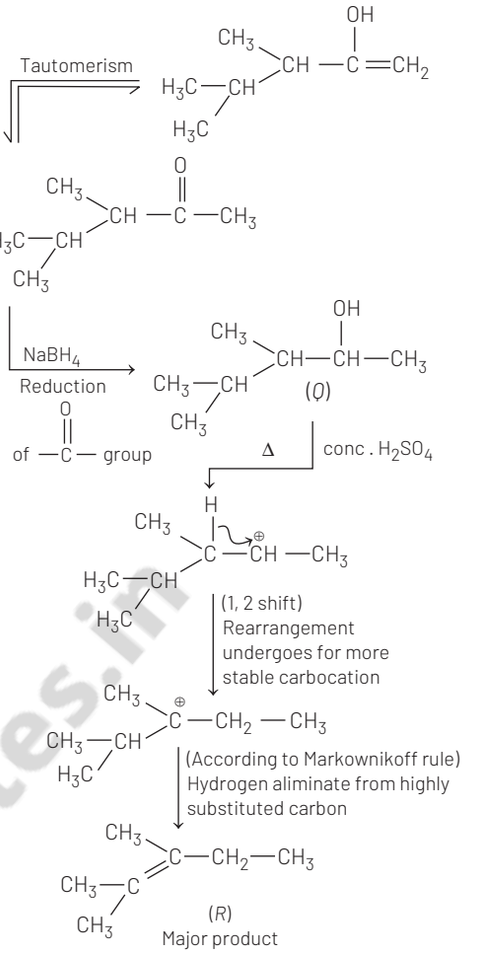
(b) 

(c) 

(d) 

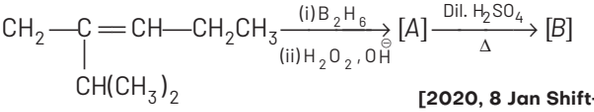
Ans. ***(c)***



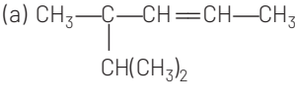


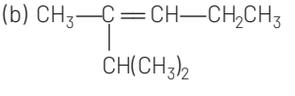
So, correct option is (c).

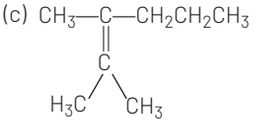
23 The major product [*B*] in the following sequence of reactions is

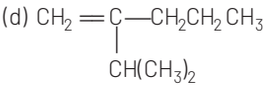


[2020, 8 Jan Shift-II]

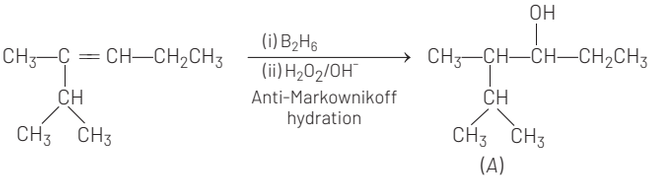
(a) 

(b) 

(c) 

(d) 

Ans. ***(c)***



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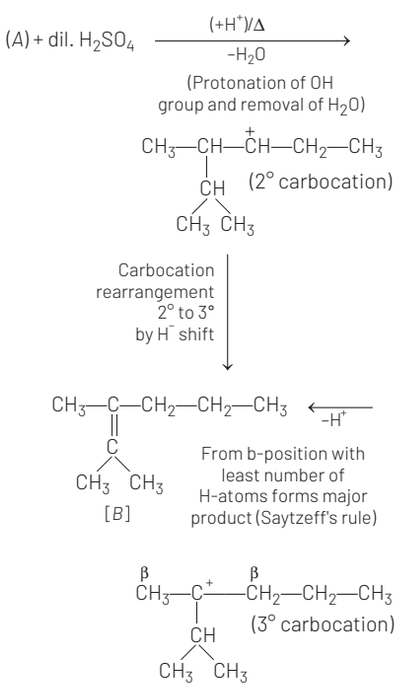
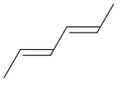
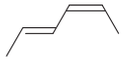


24 The correct order of heat of combustion for following alkadienes is **[2020, 9 Jan Shift-I]**

(A)  (B) 

(C)

(a) (B) < (C) < (A) (b) (A) < (B) < (C)
(c) (A) < (C) < (B) (d) (C) < (B) < (A)

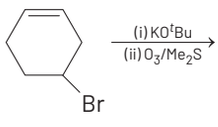
Ans. ***(b)***

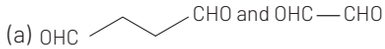
All given three alkadienes are isomers. Upon combustion, all of them gives same product.
The most stable isomer will have least heat of combustion. Between two geometrical isomers of an acyclic alkene, *trans* is more stable than *cis*. In the given options, (a) have both double bonds that are *trans*,

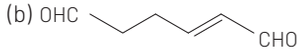
(b) have one *cis* and other one *trans* and (c) have both *cis*. So, the correct stability order of heat of combustion is

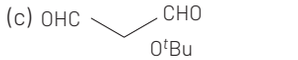
$A < B < C$.

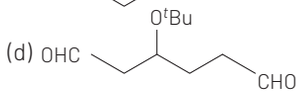
25 The major product(s) obtained in the following reaction is/are **[2019, 12 April Shift-I]**



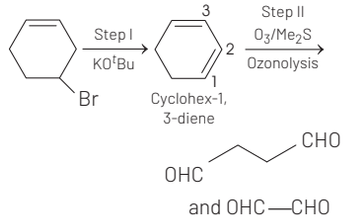
(a) 

(b) 

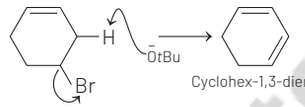
(c) 

(d) 

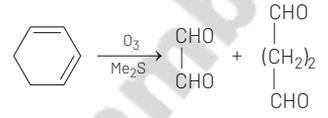
Ans. ***(a)***



In step-1 dehydrohalogenation reaction takes place. Here, hydrogen is eliminated from β-carbon and the halogen is lost from α-carbon atom. As a result diene is formed.

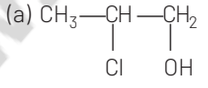


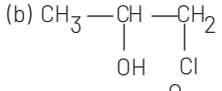
Cyclohex -1, 3-diene on ozonolysis gives butane-1, 4- dial and ethane- 1, 2- dial.

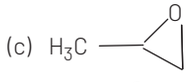


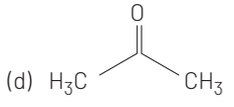
26 The major product of the following addition reaction is

$H_3C—CH=CH_2 \xrightarrow{Cl_2/H_2O}$ **[2019, 12 April Shift-I]**

(a) 

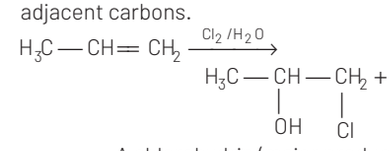
(b) 

(c) 

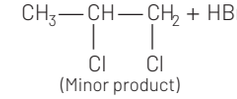
(d) 

Ans. ***(b)***

The major product of the given addition reaction is $H_3C—\underset{OH}{\underset{|}{CH}}—\underset{Cl}{\underset{|}{CH_2}}$. In this reaction, H_2O is used as a solvent and the major product of the reaction will be a *vicinal* halohydrin. A halohydrin is an organic molecule that contains both OH group and a halogen. In a *vicinal* halohydrin, the OH and halogen are bonded to adjacent carbons.

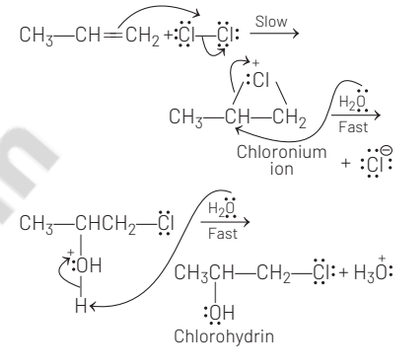


A chlorohydrin (major product)

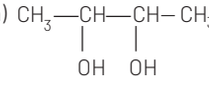


(Minor product)

The reaction proceeds through following mechanism :



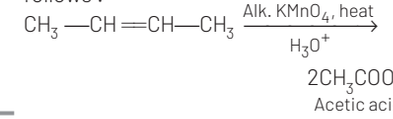
27 But-2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give **[2019, 12 April Shift-I]**

(a) 

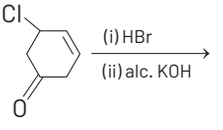
(b) one molecule of CH_3CHO and one molecule of CH_3COOH
(c) 2 molecules of CH_3COOH
(d) 2 molecules of CH_3CHO

Ans. ***(c)***

But-2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give acetic acid (CH_3COOH). Hot alkaline solution of potassium permanganate followed by acidification oxidatively cleaved alkenes. The reaction proceed as follows :



28 The major product of the following reaction is **[2019, 11 Jan Shift-I]**



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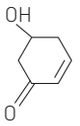
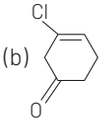
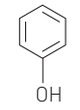
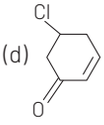
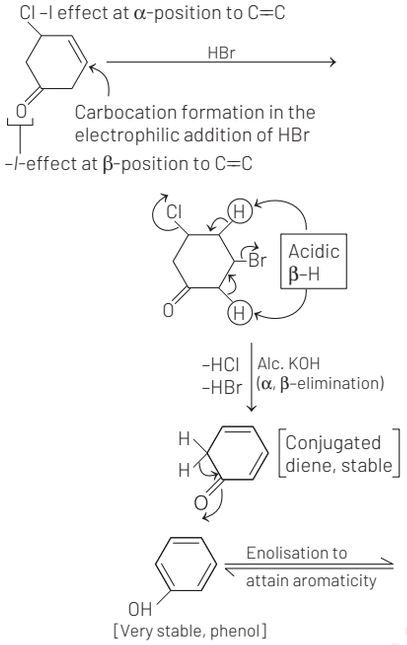
(a)  (b) 

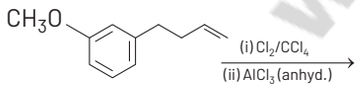
(c)  (d) 

Ans. ***(c)***

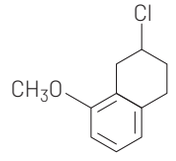
In presence of HBr, reactant containing $>C=C<$ undergoes electrophilic addition reaction and give substituted alkyl halide. On further reaction with alc. KOH, α,β-elimination takes place that give corresponding diene. The diene undergoes enolisation to give stable product (phenol).

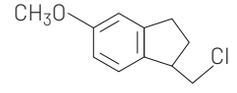


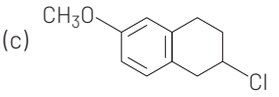
29 The major product of the following reaction is

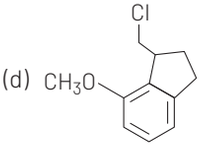


[2019, 12 Jan Shift-I]

(a) 

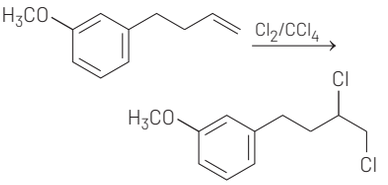
(b) 

(c) 

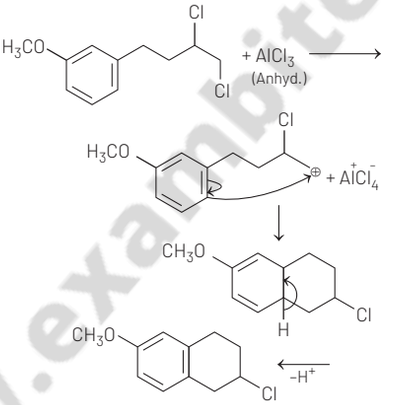
(d) 

Ans. ***(c)***

The given reactant in presence of Cl_2/CCl_4, given *vicinal* dihalide. Chlorine adds up to alkene *via* electrophilic addition reaction involving cyclic chlorinium ion formation.



The *vicinal* dihalide in presence of anhyd. $AlCl_3$ results in the formation of carbocation that rearranges itself to form a cyclic compound.

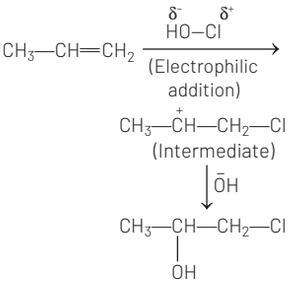


30 The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate **[JEE Main 2016]**

(a) $CH_3\overset{+}{C}HCH_2Cl$ (b) $CH_3CH(OH)\overset{+}{C}H_2$

(c) $CH_3CHCl\overset{+}{C}H_2$ (d) $CH_3\overset{+}{C}HCH_2OH$

Ans. ***(a)***

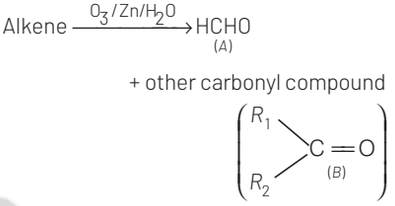


31 Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of **[AIEEE 2011]**

(a) two ethylenic double bonds
(b) a vinyl group
(c) an *iso* propyl group
(d) an acetylenic triple bond

Ans. ***(b)***

Alkenes give carbonyl compounds on ozonolysis.



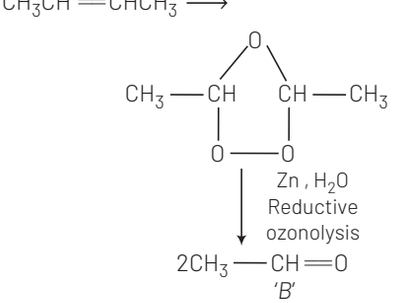
32 In the following sequence of reactions, the alkene affords the compound '*B*'

$$CH_3CH=CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$$

The compound *B* is **[AIEEE 2008]**

(a) CH_3CH_2CHO
(b) CH_3COCH_3
(c) $CH_3CH_2COCH_3$
(d) CH_3CHO

Ans. ***(d)***



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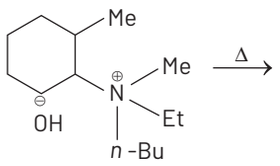
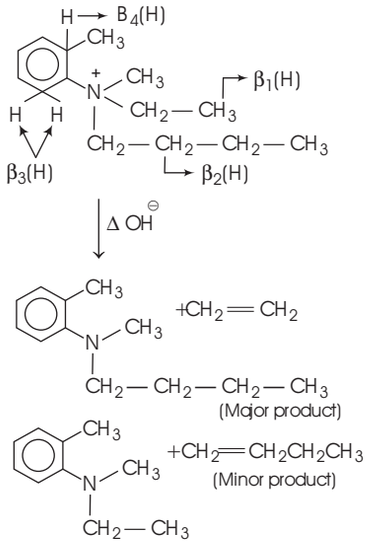
33 

The alkene formed as a major product in the above elimination reaction is **[AIEEE 2006]**

Ans. ***(b)***

Compounds bearing a quaternary nitrogen atom bonded to four alkyl groups when heated in the presence of base like OH^- undergo E_2 elimination with the formation of less substituted alkene as a major product with the loss of $\beta-H$ atom.

This type of elimination is called Hofmann elimination.

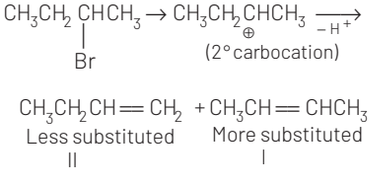


Hence, $CH_2=CH_2$ will be a major product.

24 Elimination of bromine from 2-bromobutane results in the formation of **[AIEEE 2005]**

(a) predominantly 2-butyne
(b) predominantly 1-butene
(c) predominantly 2-butene
(d) equimolar mixture of 1 and 2-butene

Ans. ***(c)***

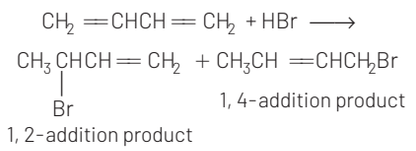


Stability of I > II, hence I is predominant.

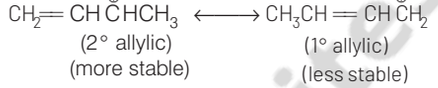
35 Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C gives predominantly **[AIEEE 2005]**

(a) 1-bromo-2-butene under kinetically controlled conditions
(b) 3-bromobutene under thermodynamically controlled conditions
(c) 1-bromo-2-butene under thermodynamically controlled conditions
(d) 3-bromobutene under kinetically controlled conditions

Ans. ***(c)***



Addition is through the formation of allylic carbocation.

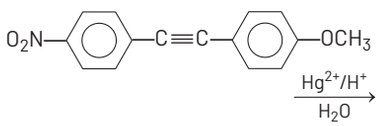


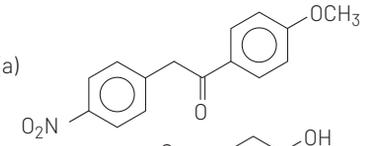
Under mild conditions (temperature ≈ – 80°C) kinetic product is the 1, 2-addition product and under vigorous conditions, (temp. ≈ 40°C) thermodynamic product is the 1, 4-addition product.

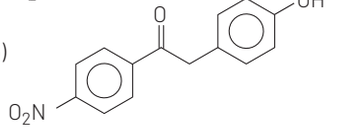
Thus, 1-bromo-2-butene is the major product under given condition.

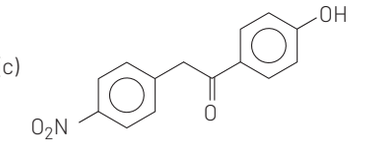
TOPIC 3
Alkynes

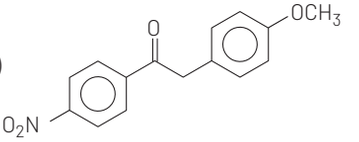
36 The major product obtained from the following reaction is **[2020, 6 Sep Shift-I]**



(a) 

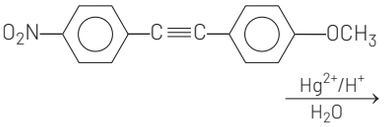
(b) 

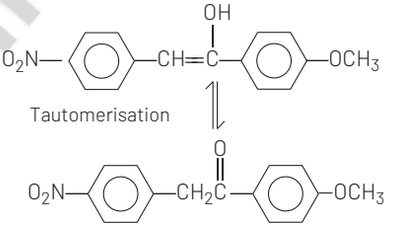
(c) 

(d) 

Ans. ***(a)***

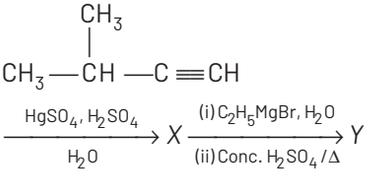
Alkynes undergo hydration in presence of $HgSO_4$ and ether are least reactive and their cleavage take place only under drastic conditions.

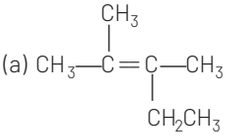


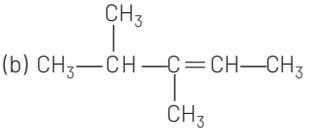


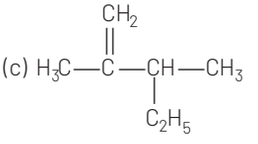
Hence, the correct option is (a).

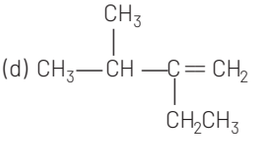
37 The major product (*Y*) in the following reaction is **[2020, 9 Jan Shift-I]**



(a) 

(b) 

(c) 

(d) 

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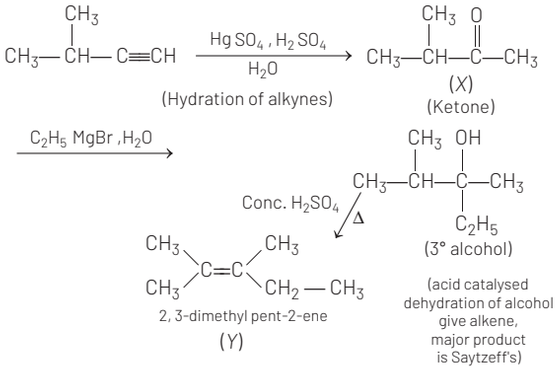
Ans. ***(a)***



38 The major product of the following reaction is

$CH_3C \equiv CH \xrightarrow[\text{(ii) DI}]{\text{(i) DCl (1 equiv.)}}$ **[2019, 9 April Shift-I]**

(a) $CH_3CD(Cl)CHD(I)$ (b) $CH_3CD_2CH(Cl)(I)$

(c) $CH_3CD(I)CHD(Cl)$ (d) $CH_3C(I)(Cl)CHD_2$

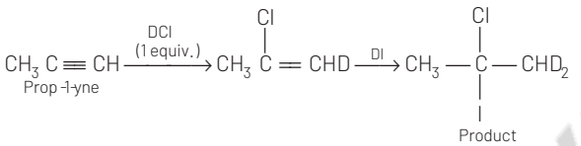
Ans. ***(d)***

The major product obtained in the given reaction is $CH_3C(I)(Cl)CHD_2$.

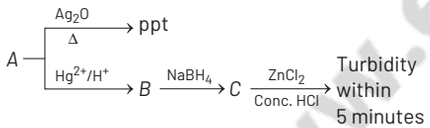
$$CH_3C \equiv CH \xrightarrow[\text{2. DI}]{\text{1. DCl (1 equiv.)}} CH_3C(I)(Cl)CHD_2$$

Addition in unsymmetrical alkynes takes place according to Markovnikov's rule.

Reaction proceed as follows :



39 Consider the following reactions,



A is **[2019, 12 April Shift-II]**

(a) $CH \equiv CH$ (b) $CH_3C \equiv CCH_3$

(c) $CH_3—C \equiv CH$ (d) $CH_2 = CH_2$

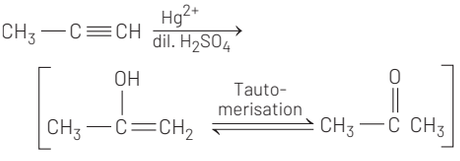
Ans. ***(c)***

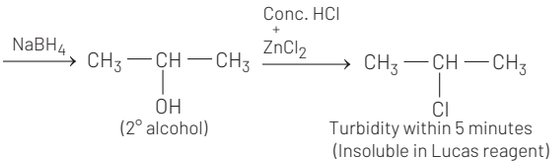
According to the given conditions, the compound should be alkyne with triple bond present at the terminal. The chemical reactions involved are as follows :

Step 1 $CH_3—C \equiv CH \xrightarrow{Ag_2O} CH_3—C \equiv C—Ag\downarrow$

Prop-1-yne (Precipitates)

Step 2





In step-1, prop-1-yne reacts with Ag_2O to form $CH_3—C \equiv C—Ag$, that forms white precipitates.

In step 2, prop-1-yne in presence of mercuric sulphate and dil·H_2SO_4 produces carbonyl compound $(CH_3)_2C=O$ which produces $(CH_3)_2CH—OH$ in presence of $NaBH_4$. 2º alcohol on reaction with Lucas reagent produces turbidity in about 5 min.

40 The major product of the following reaction is

$CH_3CH_2CH(Br)—CH_2(Br) \xrightarrow[\text{(ii) } NaNH_2 \text{ in liq. } NH_3]{\text{(i) KOH alc.}}$ **[2019, 12 Jan Shift-II]**

(a) $CH_3CH_2CH(NH_2)—CH_2(NH_2)$

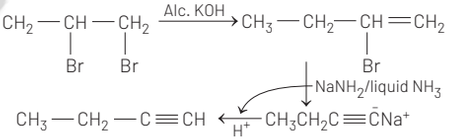
(b) $CH_3CH=CHCH_2NH_2$

(c) $CH_3CH=C=CH_2$

(d) $CH_3CH_2C \equiv CH$

Ans. ***(d)***

The reaction proceeds as :



Thus, option (d) is the correct answer.

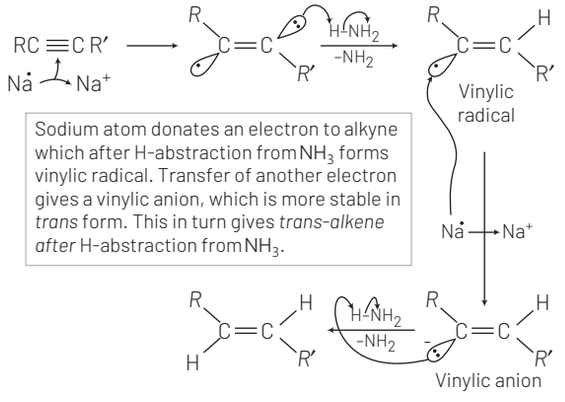
41 The *trans*-alkenes are formed by the reduction of alkynes with **[JEE Main 2018]**

(a) H_2-Pd/C, $BaSO_4$ (b) $NaBH_4$

(c) Na/liq. NH_3 (d) Sn-HCl

Ans. ***(c)***

Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry to give *trans* alkenes. The reduction is selectively *anti* since the vinyl radical formed during reduction is more stable in *trans* configuration.



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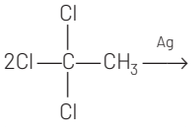
42 The major organic compound formed by the reaction of 1,1,1–trichloroethane with silver powder is **[JEE Main 2014]**

(a) acetylene (b) ethene
(c) 2–butyne (d) 2–butene

Ans. ***(c)***



(1, 1, 1–trichloroethane)

$$CH_3-C\equiv C-CH_3 + 6AgCl$$

(2-butyne)

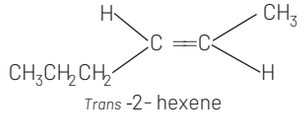
43 2-hexyne gives *trans*-2-hexene on treatment with **[AIEEE 2012]**

(a) Pt / H_2 (b) Li / NH_3
(c) $Pd / BaSO_4$ (d) $LiAlH_4$

Ans. ***(b)***

$$CH_3CH_2CH_2-C\equiv C-CH_3 \xrightarrow[\text{[Birch reduction]}]{\text{(b) } Li/NH_3}$$

2-hexyne



Trans -2- hexene

$$\text{2-hexyne} \xrightarrow{\text{(a) } Pt/H_2} \textit{n}\text{-hexane}$$

$$\xrightarrow[\text{[Lindlar's catalyst]}]{\text{(c) } Pd/BaSO_4} \textit{cis}\text{ -2-hexene}$$

$$\xrightarrow{\text{(d) } LiAlH_4} \text{no reaction}$$

44 The hydrocarbon which can react with sodium in liquid ammonia is **[AIEEE 2008]**

(a) $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$
(b) $CH_3CH_2C\equiv CH$
(c) $CH_3CH=CHCH_3$
(d) $CH_3CH_2C\equiv CCH_2CH_3$

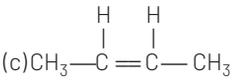
Ans. ***(b)***

Only terminal alkynes undergo reduction with sodium (Na) in liquid ammonia (NH_3). Hence, $CH_3CH_2C\equiv CH$ reacts with Na in liq. NH_3.

$$CH_3CH_2C\equiv CH \xrightarrow[\Delta]{Na/liq.\ NH_3} CH_3CH_2C\equiv C^-Na^+$$

45 The treatment of CH_3MgX with $CH_3C\equiv C-H$ produces **[AIEEE 2008]**

(a) $CH_3-CH=CH_2$
(b) $CH_3C\equiv C-CH_3$



Ans. ***(d)***

Terminal alkyne has acidic hydrogen which is enough to protonate the Grignard reagent.

$$CH_3MgX + CH_3C\equiv CH \longrightarrow CH_4 + CH_3C\equiv CMgX$$

46 Acetylene does not react with **[AIEEE 2002]**

(a) Na
(b) ammoniacal $AgNO_3$
(c) HCl
(d) NaOH

Ans. ***(d)***

$$CH\equiv CH + Na \longrightarrow CH\equiv C^-Na^+ + \frac{1}{2}H_2$$

$$CH\equiv CH + \underset{\text{(ammonical)}}{AgNO_3} \longrightarrow \underset{\text{White ppt.}}{CH\equiv C^-Ag^+}$$

$CH\equiv CH + HCl \rightarrow CH_2=CH—Cl$.
Usually occurs in the presence of Hg^{2+}.

$CH\equiv CH + NaOH \longrightarrow$ no reaction
Because of hard acid, hard base and soft acid, soft base (HASB) theory. But is reacts with $NaNH_2$.

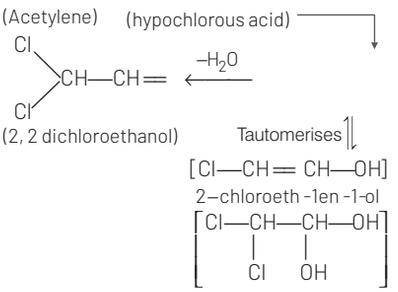
$$CH\equiv CH + NaNH_2 \longrightarrow CH\equiv C^-Na^+ \text{ feasible.}$$

47 Acetylene reacts with hypochlorous acid to form **[AIEEE 2002]**

(a) Cl_2CHCHO
(b) $ClCH_2COOH$
(c) CH_3COCl
(d) $ClCH_2CHO$

Ans. ***(a)***

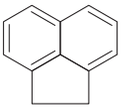
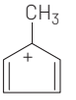
$HC\equiv CH$ + Cl—OH
(Acetylene) (hypochlorous acid)



(2, 2 dichloroethanol)

TOPIC 4
Aromatic Hydrocarbons

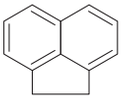
48 Which one of the following compound(s) is/are aromatic in nature ? **[2021, 1 Sep Shift-II]**

(a) 
(b)
(c) 

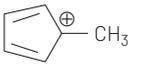
(d)

Ans. ***(a,d)***

Aromatic compounds are conjugated planar ring system having delocalised π-electron clouds and follows $(4n+2)\pi$-electron rule, i.e. Huckel's rule. $\{n = 0, 1, 2, \ldots\}$

(a) 
$\longrightarrow 10\pi e^-$ in cyclic conjugation place.
It is aromatic.

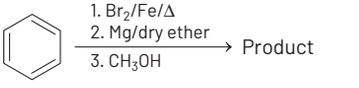
(b) $\longrightarrow 4\pi e^-$ in cyclic conjugation
It is anti-aromatic.

(c) 

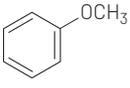
$4\pi e^-$ in cyclic conjugation.
It is anti-aromatic.

(d) $6\pi e^-$ in cyclic conjugation.
It is aromatic.

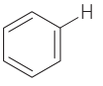
49 For the following



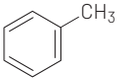
[2021, 31 Aug Shift-II]

(a) 

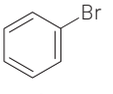
+ HMgBr

(b) 

+ Mg(OCH3)Br

(c) 

+ Mg(OH)Br

(d) 

+ Mg(OH)OCH3

Ans. ***(b)***

Benzene on reaction with Br_2/Fe give 5 bromo benzene as follows

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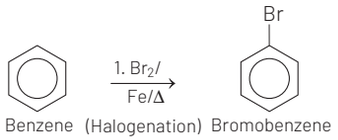
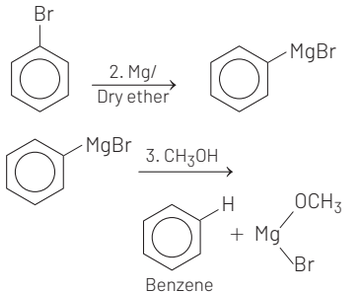


Benzene (Halogenation) Bromobenzene

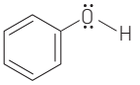
Bromobenzene on reaction with Mg / dry ether and CH_3OH gives benzene as follows



Benzene

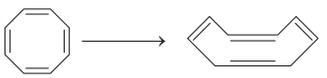
50 Which one of the following compounds is not aromatic ?

[2021, 26 Aug Shift-II]

(a)
(b)
(c)
(d) 

Ans. ***(c)***

The compound which follows Huckel's rule has planar structure is aromatic in nature.

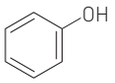
(c) 

It exist in a non-planar tube shape, so it is non-aromatic.

(a) It is aromatic in nature.

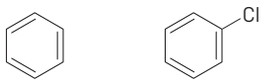
Number of $\pi e^- = 4n + 2 (n = 2) = 6\pi e^-$

(b) It is also aromatic in nature as the lone pair is in conjugation with πe^-.

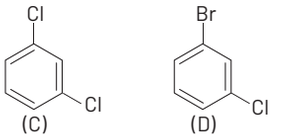
(d) 

It is aromatic in nature as it containsenzene ring.

51 The correct decreasing order of densities of the following compounds is **[2021, 25 July Shift-II]**



(A) (B)



(C) (D)

(a) (D) > (C) > (B) > (A)
(b) (C) > (D) > (A) > (B)
(c) (C) > (B) > (A) > (D)
(d) (A) > (B) > (C) > (D)

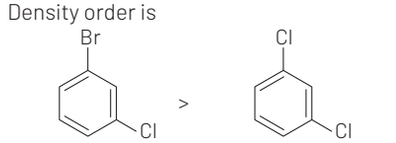
Ans. ***(a)***

At constant volume, density depends on the mass of the compound. So, density is directly proportional to mass. On moving down the group, mass increases.

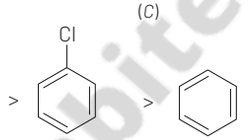
Order of decreasing density in benzene ring is

I > Br > Cl > F.

Density order is



3-chlorobromobenzene (*D*) > 3-chloro-chlorobenzene or 1, 3 dichlorobenzene (*C*)



> Chlorobenzene (*B*) > Benzene (*A*)

52 Benzene on nitration gives nitrobenzene in presence of HNO_3 and H_2SO_4 mixutre, where

[2021, 20 July Shift-II]

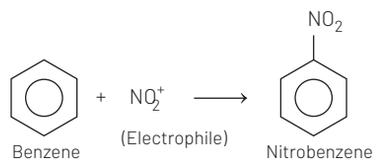
(a) both H_2SO_4 and HNO_3 act as a bases
(b) HNO_3 acts as an acid and H_2SO_4 acts as a base
(c) both H_2SO_4 and NHO_3 act as an acids
(d) HNO_3 acts as a base and H_2SO_4 acts as an acid

Ans. ***(d)***

Benzene on nitration gives nitrobenzene in presence of HNO_3 and H_2SO_4.

$$\underset{\text{(Acid)}}{H_2SO_4} + \underset{\text{(Base)}}{HNO_3} \rightleftharpoons HSO_4^{\ominus} + H_2\overset{\oplus}{N}O_3$$

$$H_2\overset{\oplus}{N}O_3 \rightleftharpoons H_2O + \overset{\oplus}{N}O_2$$

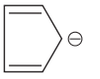
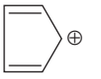
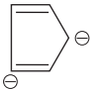


Benzene (Electrophile) Nitrobenzene

Here, H_2SO_4 acts as acid to give proton (H^+). This H^+ react with HNO_3 to give $H_2\overset{\oplus}{N}O_3$ which provide NO_2^+ (electrophile) to benzene to form nitrobenzene.

53 Which of the following is an aromatic compound?

[2021, 17 March Shift-I]

(a) 
(b) 
(c) 
(d)

Ans. ***(a)***

is an aromatic compound ($6\pi e^-$).

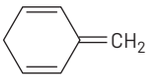
Aromatic compound possess following characteristics :

(i) Planarity
(ii) Complete delocalisation of the π-electrons in the ring.
(iii) Presence of $(4n + 2)$ π-electrons in the ring, where n is an integer ($n = 0, 1, 2 \ldots$).

That compound follow all aromatic characteristics.

54 Among the following, the aromatic compounds are

[2021, 16 March Shift-I]

(A) 
(B)
(C)
(D)

Choose the correct answer from the following options.

(a) Only (A) and (B) (b) Only (B) and (C)
(c) (B), (C) and (D) (d) (A), (B) and (C)

Ans. ***(b)***

For aromatic compounds following conditions should be satisfied

(i) planarity
(ii) complete delocalisation of π-electrons in the ring.
(iii) presence of $(4n + 2)$ π-electrons in the ring, where $n = 0, 1, 2, \ldots$. This is called Huckel rule.

e.g. $n = 0,\ 2\pi e^-$
$n = 1,\ 6\pi e^-$
$n = 2,\ 10\pi e^-$

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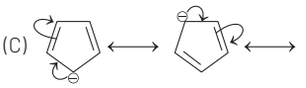
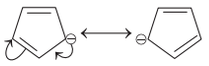
(C) 

$6pe^-$ planar

(Huckel's rule followed, i.e. aromatic)

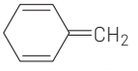


(B)

(Planar) $6pe^-$ (Huckel's rule followed, i.e. aromatic)

(C)

$4pe^-$ (Not aromatic)

(A) 

No complete delocalisation of p-electrons in the ring (Not aromatic)

55 The correct sequence of reagents used in the preparation of 4-bromo-2-nitroethyl benzene from benzene is

[2021, 25 Feb Shift-II]

(a) CH_3COCl / $AlCl_3$, Br_2 / $AlBr_3$, HNO_3 / H_2SO_4, Zn/HCl

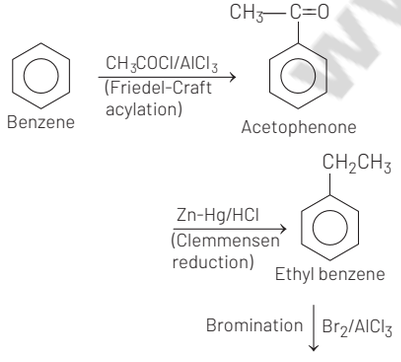
(b) CH_3COCl / $AlCl_3$, Zn-Hg/HCl, Br_2 / $AlBr_3$, HNO_3 / H_2SO_4

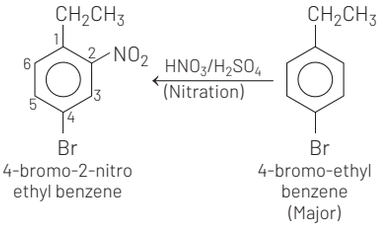
(c) Br_2 / $AlBr_3$, CH_3COCl / $AlCl_3$, HNO_3 / H_2SO_4, Zn/HCl

(d) HNO_3 / H_2SO_4, Br_2 / $AlCl_3$, CH_3COCl / $AlCl_3$, Zn-Hg/HCl

Ans. ***(b)***

Benzene on reaction with CH_3COCl / $AlCl_3$ gives acetophenone which on reduction with Zn-Hg/HCl gives ethyl benzene. Bromination of ethyl benzene give 4-bromo-ethylbenzene which upon nitration gives 4-bromo-2-nitroethyl benzene.

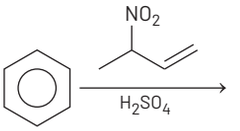


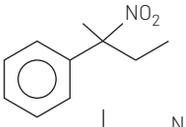


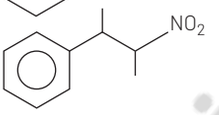
[–*I*-effect of Br directs NO_2^- at its *meta*-position]

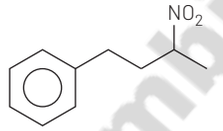
So, option (b) is the correct sequence of reagents used.

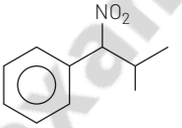
56 The major product of the following reaction is **[2021, 25 Feb Shift-II]**



(a) 

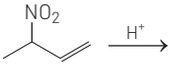
(b) 

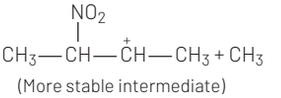
(c) 

(d) 

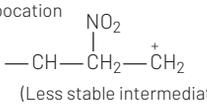
Ans. ***(b)***

The reaction take place as follows :

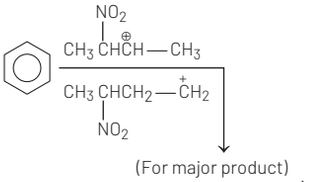
Step I 

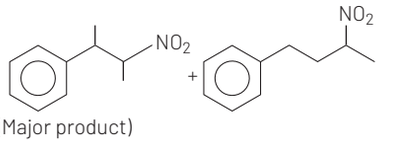


(More stable intermediate)
2° carbocation

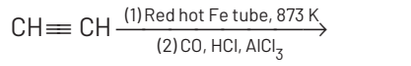


(Less stable intermediate)
1° carbocation

Step II 



57 Consider the following chemical reaction.

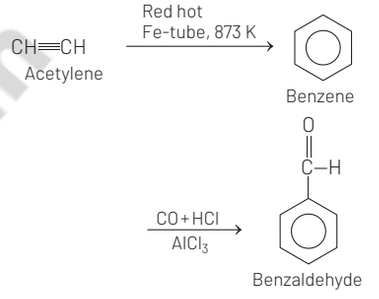


Product

The number of sp^2 hybridised carbon atom(s) present in the product is ... . **[2021, 25 Feb Shift-I]**

Ans. ***(7)***

The reaction take place as follows



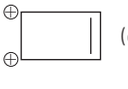
Every carbon atom found in benzaldehyde (6 carbon in benzene ring +1 in aldehyde group), forms three bonds with neighbouring atoms-(one double bond + two single bond). Therefore, in benzaldehyde total number of sp^2 'C' are 7.

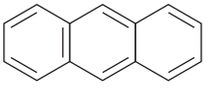
58 Which one of the following compounds is non-aromatic ?

[2021, 24 Feb Shift-II]

(a)

(b)

(c) 

(d) 

Ans. ***(a)***

Compound, which obey Huckel rule, $(4n+2)\pi$ is called aromatic compound.

Compound, which obey $4n\pi$ rule, is called anti-aromatic compound.

Compound which contain one or more sp^3 carbon in its structure is called non-aromatic compound.

The nature of following ions/compounds are as follows :

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(a) sp^3 Carbon

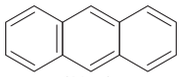
⟶ Non-aromatic

(b) $(6e^-)$

⟶ Aromatic (follow Huckel's rule)

(c) $(2e^-)$

⟶ Aromatic (follow Huckel's rule)

(d) 

$(14e^-)$

⟶ Anthracene ⟶ Aromatic

Only (a) is non-aromatic and rest all are aromatic.

59 The reaction of $H_3N_3B_3Cl_3$ (*A*) with $LiBH_4$ in tetrahydrofuran gives inorganic benzene (*B*). Further, the reaction of (*A*) with (*C*) leads to $H_3N_3B_3(Me)_3$. Compounds (*B*) and (*C*) respectively, are **[2020, 9 Jan Shift-II]**

(a) diborane and MeMgBr
(b) boron nitride and MeBr
(c) borazine and MeBr
(d) borazine and MeMgBr

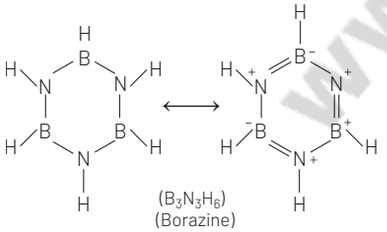
Ans. ***(d)***

Road map of the given reactions is as follows :

$H_3N_3B_3Cl_3$ (*A*) $\xrightarrow[(THF)]{+LiBH_4}$ (*B*), Inorganic benzene

(*A*) $\xrightarrow{+(C)}$ $H_3N_3B_3(Me)_3$

Complete reactions are as follows :



$(B_3N_3H_6)$ (Borazine)

60 The number of sp^2-hybrid orbitals in a molecule of benzene is **[2020, 9 Jan Shift-II]**

(a) 24 (b) 12 (c) 18 (d) 6

Ans. ***(c)***

In benzene, every carbon atom is sp^2-hybridised.

Each sp^2-hybridised atom has three sp^2 hybrid orbitals.

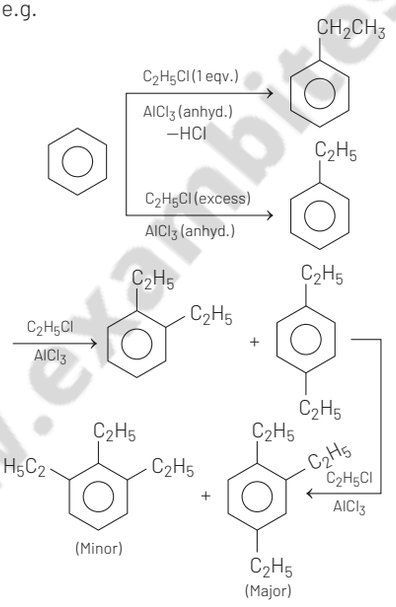
$\therefore$ Total number of sp^2 hybrid orbitals in a molecule of benzene is $= 6 \times 3 = 18$

61 Polysubstitutiion is a major drawback in **[2019, 8 April Shift-II]**

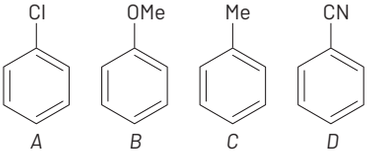
(a) Friedel-Craft's alkylation
(b) Reimer-Tiemann reaction
(c) Friedel-Craft's acylation
(d) Acetylation of aniline

Ans. ***(a)***

Through aromatic electrophilic substitution mechanism (ArS_E2) when mono-alkylation (Friedel- Craft's reaction) is performed, we get mono-alkylated benzene. As, the alkyl group is ring activating (towards ArS_E2) in nature, again *o*- and *p*-substituted alkyl benzene will be obtained and so on. e.g.



62 The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is **[2019, 9 April Shift-I]**



(a) $A < B < C < D$ (b) $B < C < A < D$
(c) $D < A < C < B$ (d) $D < B < A < C$

Ans. ***(c)***

Aromatic electrophilic substitution reactions are fast in those compounds in which the attacking site possess high electron density. Electron withdrawing groups (EWGs) reduces the electron density in the benzene ring due to its strong $-I$ effect and makes further substitution difficult. Hence, called as deactivating groups. While electron releasing groups (ERGs) increases the electron density in the benzene due to resonance. Therefore, activates the benzene ring for the attack by an electrophile.

Hence, called as activating groups.

In given options,

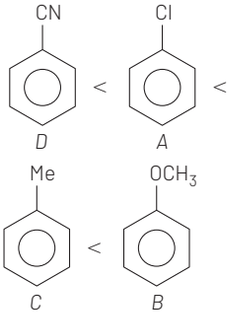
Activating groups are

$$-CH_3 < \underset{\text{Strong } +R\text{-effect}}{-\ddot{O}CH_3}$$
$$(+I, +R)$$

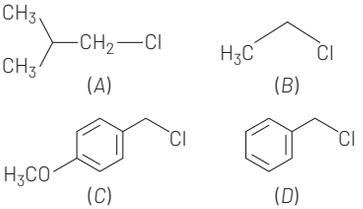
Deactivating groups are

$$-CN > -Cl$$
$$\text{Strong } -I\text{-effect} \quad (-I > -R)$$

So, the correct order is



63 Increasing order of reactivity of the following compounds for S_N1 substitution is **[2019, 9 April Shift-II]**



(a) $(A) < (B) < (D) < (C)$
(b) $(B) < (C) < (D) < (A)$
(c) $(B) < (A) < (D) < (C)$
(d) $(B) < (C) < (A) < (D)$

Ans. ***(c)***

Reactivity of substitution nucleophilic unimolecular (S_N1) reaction depends on the formation of carbocation. Greater the stability of carbocation, greater will be its ease of formation of alkyl halide

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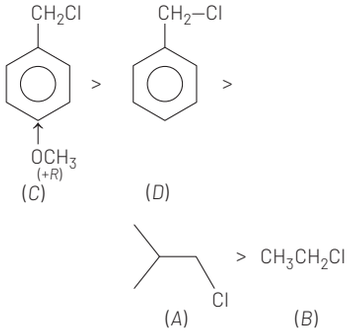
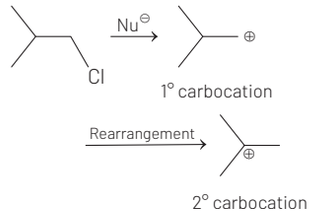
and faster will be the rate of reaction. So, the correct order of (S_N1) reactivity is

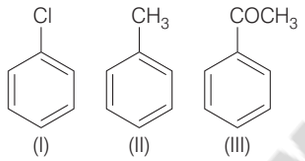


In compound *C*, the carbocation formed is stabilised by activating group (—OCH_3). Compound *D* forms benzyl carbocation (C_6H_5—CH_2^+) that is stabilised by resonance. Compound *A* produces a primary carbocation that further rearranges itself to secondary carbocation.



Compound *B* produces primary carbocation which is least stable among all the given options.

64 The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reaction is **[2019, 10 April Shift-I]**



(a) III < I < II (b) II < I < III
(c) III < II < I (d) I < III < II

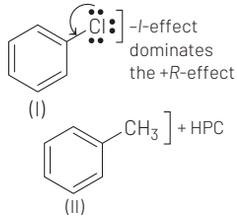
Ans. ***(a)***

Key Idea In electrophilic aromatic substitution (*Ar* S_E2) reaction, the aromatic (benzene nucleus here) compound (substrate) acts as a nucleophile which gets attacked by an electrophile in the rate determining step (rds).

Higher electron density on the nucleophile, i.e. benzene nucleus will fasten the rate of the reaction.

Electron-donating groups (EDG) will increase electron density in benzene nucleus by any or both of their +*R*/+*M* and hyperconjugative (HPC) effects.

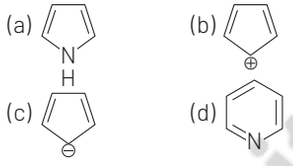
Now, let us consider the given substrte.



As –*R* effect is more powerful than –*I* effect, the order of their reactivity, towards an electrophile will be

III < I < II
(–*R*) < (–*I*>+*R*) < (+ HPC)

65 Which of the following compounds is not aromatic? **[2019, 9 Jan Shift-II]**

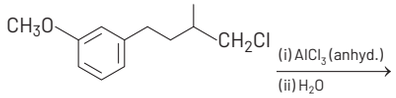


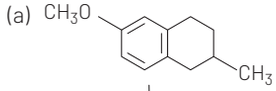
Ans. ***(b)***

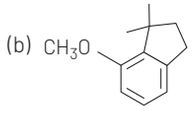
Aromaticity of a compound can be decided by Huckel's rule. In cyclopentadienyl cation (b), resonance takes place as follows:

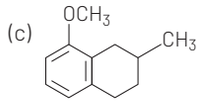
Hence, is anti-aromatic does not follow Huckel's rule as it has conjugated 4π-electron ($4n\,\pi$, $n = 1$) system. Rest of the species are aromatic as each of them belongs to 6π-electron [$(4n + 2)\,\pi$, $n = 1$] system.

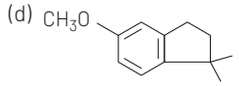
66 The major product of the following reaction is



(a) 

(b) 

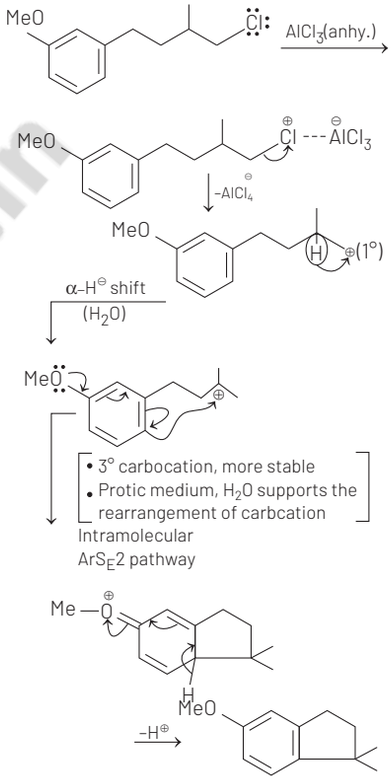
(c) 

(d) 

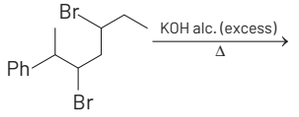
[2019, 10 Jan Shift-I]

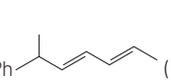
Ans. ***(d)***

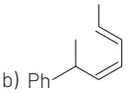
In the given reaction, $AlCl_3$ act as Lewis acid and helps in generation of carbocation. The resulting carbocation (1°) rearranges itself to stable carbocation (3°).

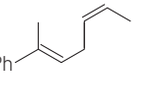


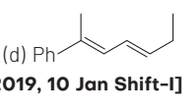
67 The major product of the following reaction is



(a) Ph 

(b) Ph 

(c) Ph 

(d) Ph 

[2019, 10 Jan Shift-I]

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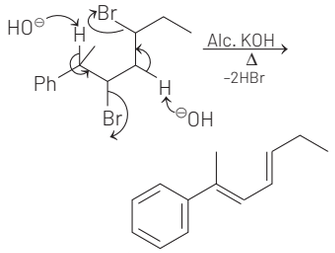
Ans. ***(d)***

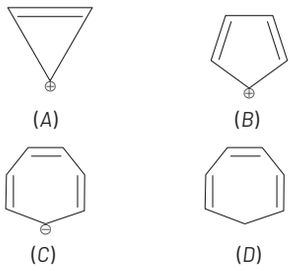
The reaction follows α,β-elimination mechanism to give a more substituted stable alkene as a major product. As the substrate is a α,γ -dibromo (1, 3-) compound it gives a conjugated diene.



(It is very stable because the conjugated diene system present. It is further conjugated with the benzene ring.)

68 Which compound (s) out of the following is/are not aromatic?

[2019, 11 Jan Shift-I]



(a) (*B*), (*C*) and (*D*) (b) (*C*) and (*D*)
(c) (*B*) (d) (*A*) and (*C*)

Ans. ***(a)***

A compound is considered to be aromatic, if it follows three rules:

- Must be cyclic and planar.
- Must have conjugated system in it.
- It must follow Huckel rule which states that number of π-electrons $=(4n+2)$

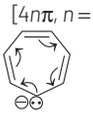
(*A*) $\Rightarrow 2\pi$-e^- system

$[(4n+2)\pi, n=0]$

$\Rightarrow$ Aromatic

(*B*) $\Rightarrow 4\pi$-e^- system

$[4n\pi, n=1] \Rightarrow$ Anti-aromatic

(*C*) 

$\Rightarrow 8\pi$-e^- system $[4n\pi, n=2]$

$\Rightarrow$ Anti-aromatic

(*D*)

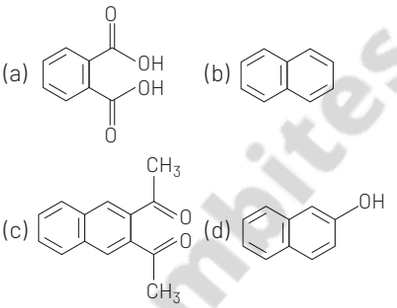
sp^3

$\Rightarrow$ The sp^3-carbon does not support conjugation and also devoids planarity.

$\Rightarrow$ Non-aromatic

69 Among the following four aromatic compounds, which one will have the lowest melting point?

[2019, 12 Jan Shift-II]



Ans. ***(b)***

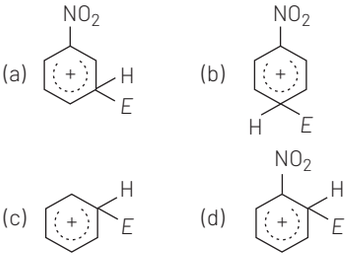
Melting point of a compound depends on size and force of attraction between the molecules. Compound (c) has largest size and also possess weak intermolecular association due to dipole-dipole interactions.

Compound (a) is a dicarboxylic acid and possess high melting point due to intermolecular hydrogen bonding.

As a result, it exist as associated molecule. Compound (d) is an alcohol and possess intermolecular H-bonding. No interactions are present in hydrocarbon (naphthalene) compound (b).

Hence, melting point is lowest for naphthalene ($\simeq 80°$ C), i.e. compound (b).

70 The electrophile, E^+ attacks the benzene ring to generate the intermediate σ-complex. Which of the following σ-complex is of lowest energy? **[AIEEE 2008]**



Ans. ***(c)***

—NO_2 being an electron withdrawing group destabilises the carbocation by decreasing electron density form σ – complex. Thus, the presence of NO_2 group on a benzene ring of σ – complex decreases their stability. However, the carbocation (*c*) does not contain any —NO_2 group.

Thus, it would be highly stable than other σ-complexes. Hence, σ-complex (*c*) is of lowest energy.

71 Presence of a nitro group in a benzene ring

(a) activates the ring towards electrophilic substitution
(b) renders the ring basic
(c) deactivates the ring towards nucleophilic substitution
(d) deactivates the ring towards electrophilic substitution

[AIEEE 2007]

Ans. ***(d)***

— NO_2 group withdraw electron from the ring, thus shows –*M* effect and makes ring more electron deficient.

Hence, — NO_2 deactivates the ring for electrophilic substitution.

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24

Organic Compounds Containing Halogens

TOPIC 1
Haloalkane

01 In the following sequence of reactions, **[2021, 01 Sep Shift-II]**

$$C_3H_6 \xrightarrow{H^+/H_2O} A \xrightarrow[\text{dil. KOH}]{KIO} B + C$$

The compounds *B* and *C* respectively are

(a) CI_3COOK, HCOOH

(b) CI_3COOK, CH_3I

(c) CH_3I, HCOOK

(d) CHI_3, CH_3COOK

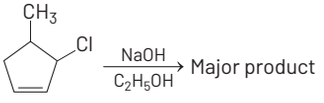
Ans. ***(d)***

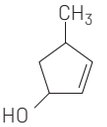
Propene (C_3H_6) undergoes acidic hydrolysis to give *A* which is 2° alcohol. This alcohol undergoes iodoform reaction in presence of KIO and dil. KOH to give iodoform alongwith potassium salt of carboxylic acid.

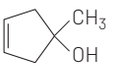
This reaction is known as iodoform test.

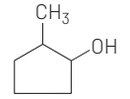
$$\underset{\substack{\text{Propene}\\(C_3H_6)}}{CH_3-CH=CH_2} \xrightarrow[\text{Acidic hydrolysis}]{H^+/H_2O} \underset{\substack{\text{Propan-2-ol}\\(A)}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3} \xrightarrow[\text{Iodoform}]{KIO/Dil.\ KOH} \underset{\substack{\text{Potassium salt of ethanoic acid}\\\text{(Postassium acetate)}\\(C)}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O^{\ominus}K^{\oplus}} + \underset{\substack{\text{Iodoform}\\(B)}}{CHI_3}$$

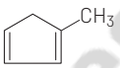
02 The major product of the following reaction is **[2021, 31 Aug Shift-II]**



(a) 

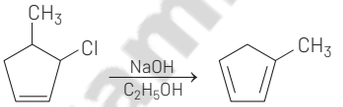
(b) 

(c) 

(d) 

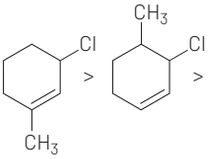
Ans. ***(d)***

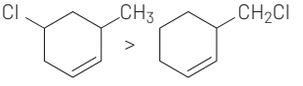
In the given reaction E2 elimination reaction takes place in which two substituents are removed from a molecule to form double bond (alkene).

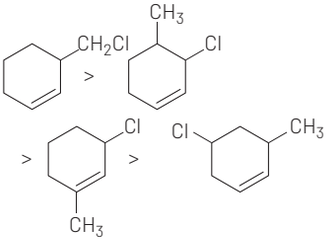


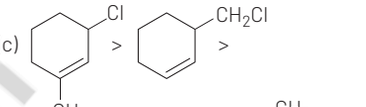
1-methyl cyclopent-1-3-diene (Major product)

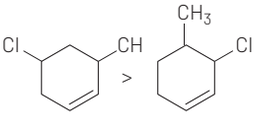
03 The correct order of reactivity of the given chlorides with acetate in acetic acid is **[2021, 31 Aug Shift-I]**

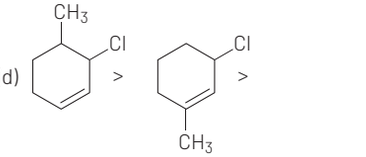
(a) 

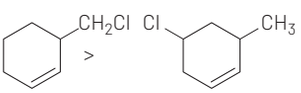


(b) 

(c) 

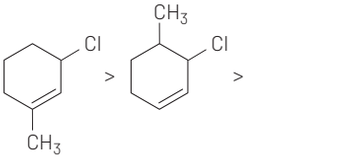


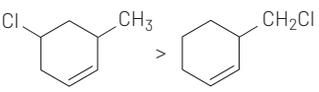
(d) 



Ans. ***(a)***

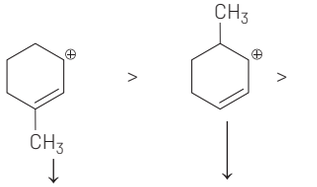
The correct order of reactivity of chlorides with acetate in acetic acid is





The given chlorides undergoes S_N1 reaction. So, as the stability of carbocation formed increases, rate of reaction increases.

Stability of carbocation is as follows



Allylic carbocation +2α-H

Allylic carbocation +1α-H

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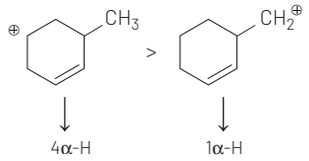
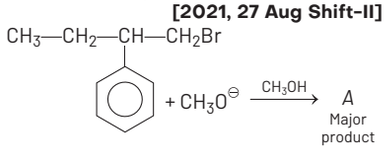
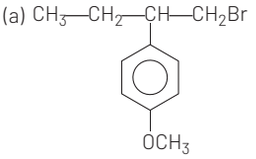


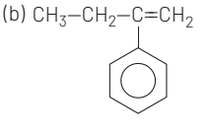
Hence, correct option is (a).

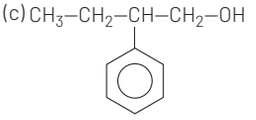
04 The major product (*A*) formed in the reaction given below is

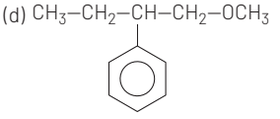
[2021, 27 Aug Shift-II]



(a) 

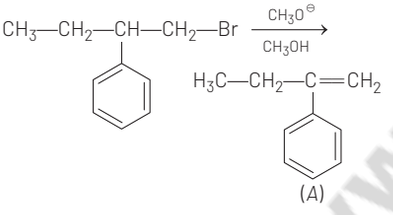
(b) 

(c) 

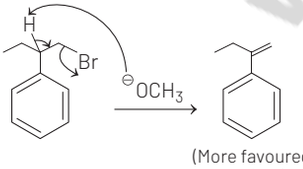
(d) 

Ans. ***(b)***

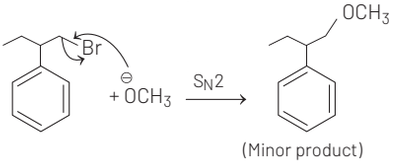
On reaction of haloalkane with methoxide ion, alkene is formed.



Mechanism



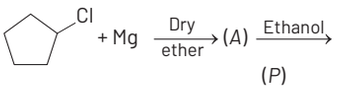
- $\overset{\ominus}{O}CH_3$ will act as a base due to its small size and high electron density and therefore, abstracts proton to form double bond which is in conjugation with aromatic ring.
- The $\overset{\ominus}{O}CH_3$ when acts as nucleophile undergoes nucleophilic substitution and replaces $Br^{\ominus}$ to form ether, which is a minor product.



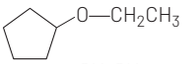
So, option (b) is correct.

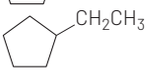
05 In the following sequence of reactions the *P* is

[2021, 27 Aug Shift-I]



(a)

(b) 

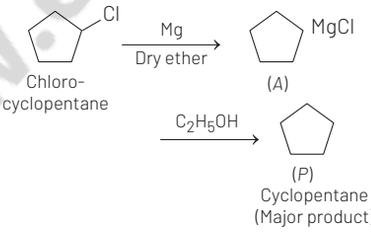
(c) 

(d)

Ans. ***(a)***

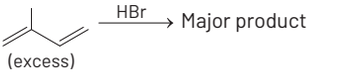
In the first step, Grignard reagent is obtained. In the second step, acid-base reaction occurs. Due to presence of an acidic hydrogen in alcohol, neutralisation reaction takes place that produces alkane and water.

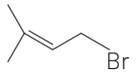
The reaction is

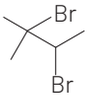


06 The major product formed in the following reaction is

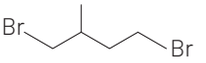
[2021, 26 Aug Shift-I]



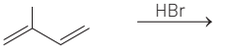
(a) 

(b) 

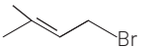
(c)

(d) 

Ans. ***(a)***



2-methylbut-1,3-diene

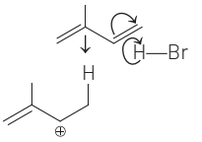


1-bromo 3-methylbut-2-ene

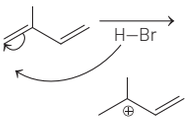
This addition is known as 1, 4-addition.

Mechanism This reaction can undergoes two pathways

Path *A*

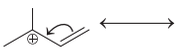


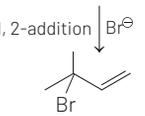
2° carbocation

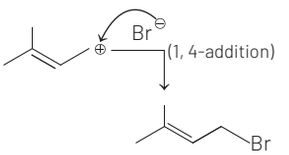
Path *B* 

3° carbocation

Out of the two intermediates formed in two paths, the path *B* intermediate is more stable as it has more stable carbocation. So, major product will be formed because of path *B*.







1, 2-addition product is formed at low temperature and will be less stable as double bond is less substituted. 1, 4-addition is thermodynamically stable product as double bond is more substituted. As diene is in excess and HBr is limited in reaction, so diene cannot be formed. So option (b) is incorrect.

07 Excess of isobutane on reaction with Br_2 in presence of light at 125°C gives which one of the following, as the major product?

[2021, 26 Aug Shift-I]

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(a) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_2-Br$

(b) $CH_3-\underset{\underset{CH_2Br}{|}}{CH}-CH_2Br$

(c) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Br$

(d) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br$

Ans. ***(d)***

Excess of isobutane reacts with Br_2 in presence of light at 125°C gives 2-bromo-2-methyl propane as major product.

$$CH_3-\underset{\text{Isobutane (excess)}}{\underset{\underset{CH_3}{|}}{CH}}-CH_3 \xrightarrow[h\nu\,/\,125\,^\circ C]{Br_2} H_3C-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2-bromo-2-methyl propane

Mechanism The above reaction is halogenation of alkane *via* free radical substitution reaction.

Initiation step

$$Br_2 \xrightarrow{h\nu} Br^\bullet + Br^\bullet$$

Propagation step

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-H + Br^\bullet \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^\bullet}} + HBr$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^\bullet}} + Br_2 \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + Br^\bullet$$

Termination step

$$Br^\bullet + Br^\bullet \longrightarrow Br_2$$

$$Br^\bullet + H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^\bullet}} \longrightarrow \underset{\text{(Major product)}}{H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br}$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^\bullet}} + H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^\bullet}} \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Reactivity order of abstraction of H towards bromination of alkane as more stable alkyl free radical is formed as follows

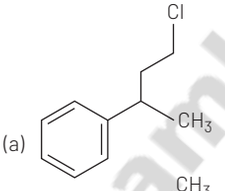
$$3°H > 2°H > 1°H$$

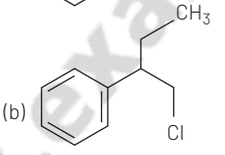
Since, isobutane is in excess, so dibromination of single isobutane is not favourable reaction. This make (a) and (b) incorrect options.

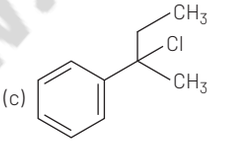
08 Reaction of Grignard reagent, C_2H_5MgBr with C_8H_8O followed by hydrolysis gives compound '*A*' which reacts instantly with Lucas reagent to give compound *B*, $C_{10}H_{13}Cl$.

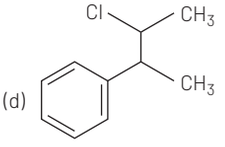
The compound *B* is

[2021, 18 March Shift-I]

(a) 

(b) 

(c) 

(d) 

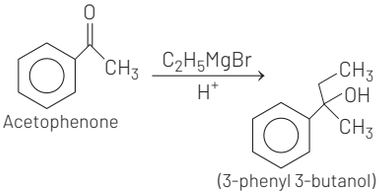
Ans. ***(c)***

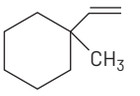
Reaction of Grignard reagent, C_2H_5MgBr with C_8H_8O followed by hydrolysis gives compound *A*, which reacts instantly with Lucas reagent to give compound *B*, $C_{10}H_{13}Cl$. It will show instant turbidity.

Step (i) $C_8H_8O \xrightarrow[H^+]{C_2H_5MgBr} (A)$

Step (ii) $(A) \xrightarrow{\text{Lucas reagent}} (B)\ C_{10}H_{13}Cl$

Complete reaction is as follows

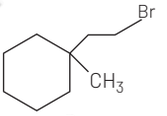


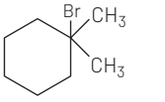
09 

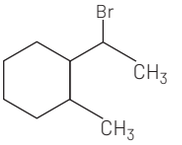
$\xrightarrow[CCl_4]{Br}$ *A* (Major product)

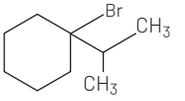
[2021, 17 March Shift-I]

Product *A* is

(a) 

(b) 

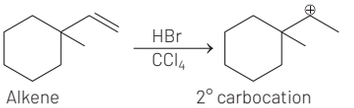
(c) 

(d) 

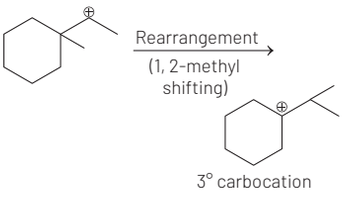
Ans. ***(d)***

Alkene undergoes electrophilic addition with HBr to give a major product by Markownikoff rule by S_N1 mechanism.

Step 1. Addition of electrophile to form carbocation.



2° carbocation undergoes methyl shift to form more stable 3° carbocation.



Step 2. Attack of nucleophile on carbocation.

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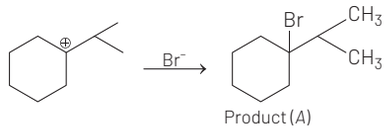
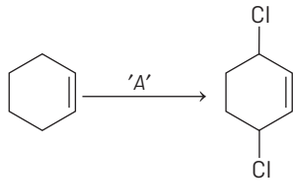


Product (*A*)

10



Identify the reagent(s) '*A*' and condition(s) for the reaction:

[2021, 16 March Shift-II]

(a) *A* = HCl, anhydrous $AlCl_3$

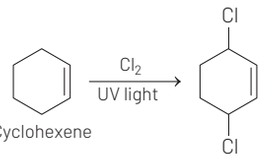
(b) *A* = HCl, $ZnCl_2$

(c) *A* = Cl_2, UV light

(d) *A* = Cl_2, dark, anhydrous $AlCl_3$

Ans. ***(c)***

The reaction can be achieved by Cl_2 /UV light (*A*). Given, reaction follows free radical substitution mechanism.



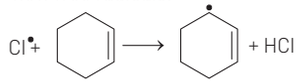
Cyclohexene

1, 4-dichloro cyclohexene

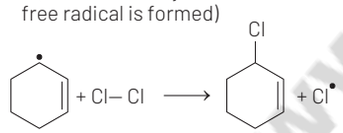
Mechanism

(I) Initiation : This involves formation of radicals.

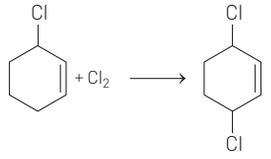
(II) Propagation : Reactive free radicals react with stable molecules to form new free radicals.



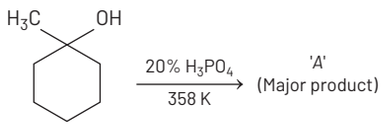
(More stable allylic free radical is formed)

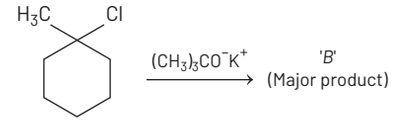


Similarly second Cl atom is also attached at allylic position.



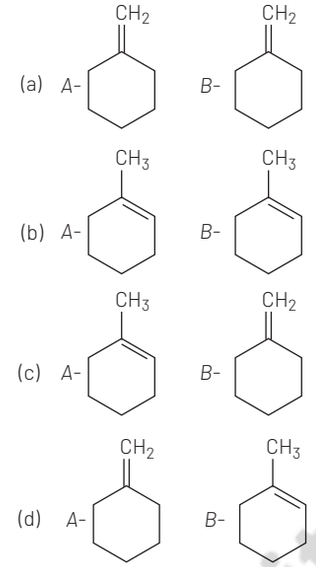
11





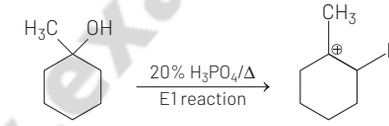
The product *A* and *B* formed in above reactions are

[2021, 16 March Shift-I]



Ans. ***(c)***

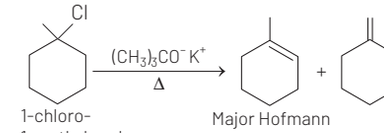
Alcohols undergo dehydration (removal of water molecule) in the presence of protic acids (conc. H_2SO_4, H_3PO_4) at high temperature to give Saytzeff alkene (more alkylated) as major product.



1-methyl cyclohexanol

Major Saytzeff alkene (A) (More alkylated) (*B*)

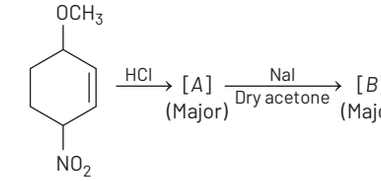
Bulky bases like *tert*-butoxide, due to steric hindrance, a bulky base abstracts a less hindered proton, that leads to formation of the less substituted product as, the major one, called the Hofmann product.

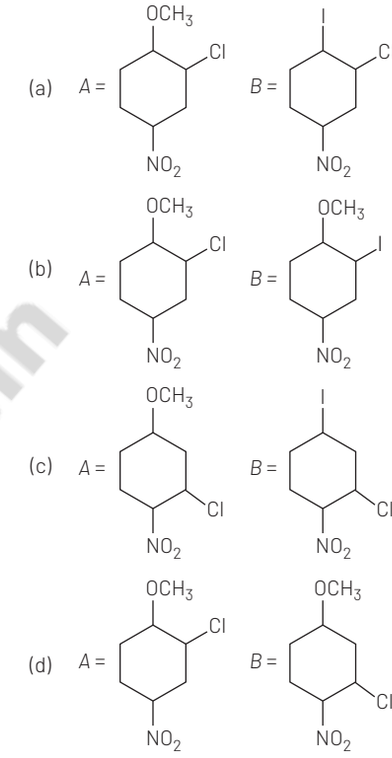


1-chloro-1-methyl cyclo hexane

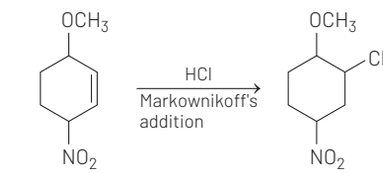
Major Hofmann alkene

12 Identify *A* and *B* in the chemical reaction. **[2021, 25 Feb Shift-I]**



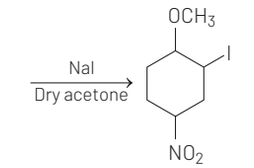


Ans. ***(b)***



4-methoxy-nitro-hex-2-ene

3-chloro-4-methoxy nitrohexane (*A*)



3-iodo-4-methoxy nitro hexane (*B*)

Ist reaction is Markownikoff's addition of HCl on double bond while 2nd reaction is halide substitution by Finkelstein reaction in which chlorine get displaced by iodine.

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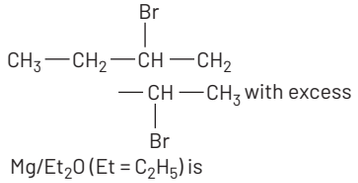
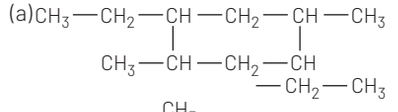
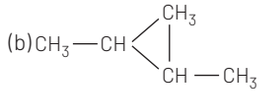
13 The product formed in the first step of the reaction of

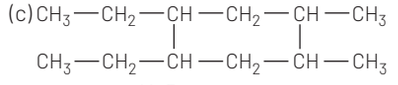


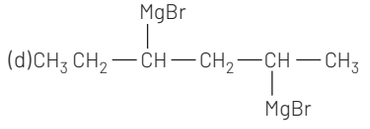
Mg/Et_2O (Et = C_2H_5) is

[2021, 24 Feb Shift-I]

(a) 

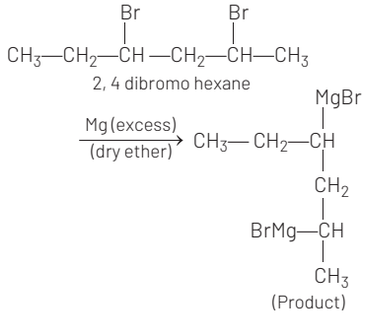
(b) 

(c) 

(d) 

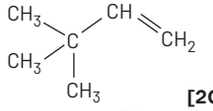
Ans. ***(d)***

Here, in first step only one mole of Mg/Et_2O attacks on bromine and form two 2MgBr in the first step.



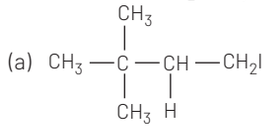
On further moving in the reaction, two MgBr are eliminated to form alkene in respective positions.

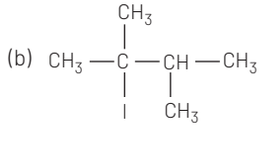
14 What is the major product formed by HI on reaction with

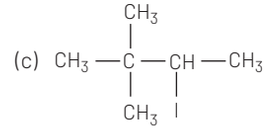


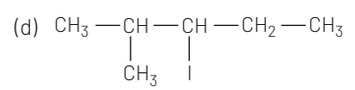
?

[2021, 24 Feb Shift-I]

(a) 

(b) 

(c) 

(d) 

Ans. ***(b)***

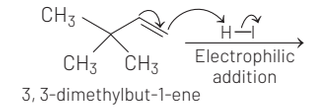
The major product formed is 2-iodo-2, 3-dimethylbutane. Steps involved in the reaction are as follows :

Step 1 It is electrophilic addition reaction, π-bond of alkene attack H^+ ion of HI and form more stable carbocation.

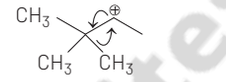
Step 2 Formation of more stable 3° carbocation take place by 1, 2 shifting of —Me group.

Step 3 Direct addition of $I^{\ominus}$ ion .

Mechanism

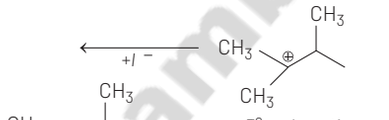


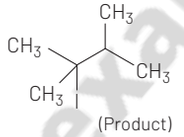
3, 3-dimethylbut-1-ene



1° carbocation

1,2-shifting of CH_3^-





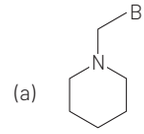
(Product)

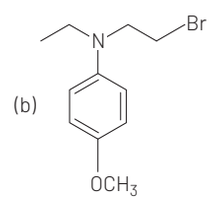
2-iodo-2,3-dimethylbutane

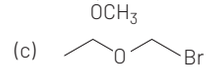
3° carbocation (More stable) (Carbocation stable by 6α-H)

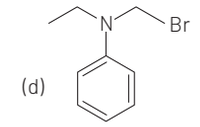
15 Which of the following compounds will form the precipitate with *aq*. $AgNO_3$ solution most readily?

[2020, 4 Sep Shift-II]

(a) 

(b) 

(c) 

(d) 

Ans. ***(b)***

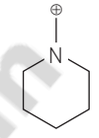
All given species in the question are alkyl halide. They react with aqueous $AgNO_3$ solution with different rate.

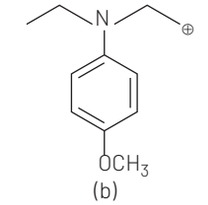
Reaction undergoes as follows:

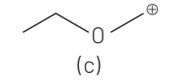
$$R—X + AgNO_3(aq) \xrightarrow{RDS} R^+ + \underset{\text{Precipitate}}{AgX}$$

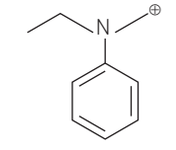
Hence, rate precipitate formation of Ag*X* depends on stability of carbocation (R^+).

In the given question all formed carbocation will be

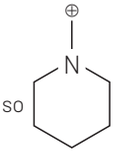
(a) 

(b) 

(c) 

(d) 

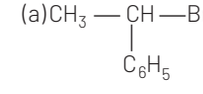
Among the above given option(s) carbocation (a) is most stable due to

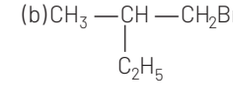
stronger +*M* effect, so  give

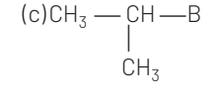
precipitate with aqueous $AgNO_3$ solution most readily.

16 Which of the following compounds will show retention in configuration on nucleophilic substitution by OH^- ion?

[2020, 2 Sep Shift-I]

(a) 

(b) 

(c) 

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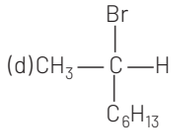
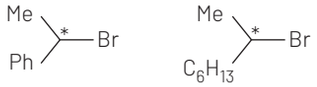
(d) 

Ans. ***(b)***

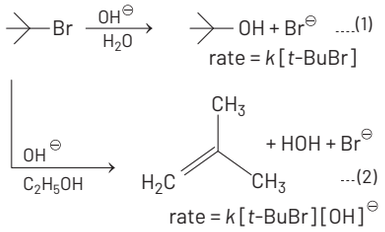
In (a) and (d), carbon atoms bearing the leaving group (Br atom) are chiral. So, their configurational change will take place with OH^- ion by S_N2 or S_N1 pathway.



In (c), $(CH_3)_2CH$—Br does not have any chiral centre. So, no comment on configuration will arise with (c).

In option (b), the α-carbon (with respect to —CH_2Br with which S_N2 reaction will take place) is only chiral. This α-carbon remains unaffected in S_N2 pathway. So, it will show retention in configuration.

17 Consider the reaction sequence given below :



Which of the following statements is true?

[2020, 2 Sep Shift-II]

(a) Changing the base from OH^- to ^-OR will have no effect on reaction (2)

(b) Changing the concentration of base will have no effect on reaction (1)

(c) Doubling the concentration of base will double the rate of both the reactions

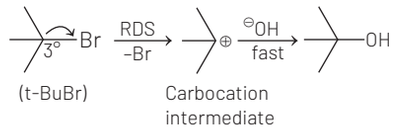
(d) Changing the concentration of base will have no effect on reaction (2)

Ans. ***(b)***

Reaction (1)

Rate = k[t-BuBr], it is a first order nucleophilic substitution reaction (S_N1), so, rate of this reaction will depend only on the concentration of the substrate, i.e. t-BuBr.

So, option (b) is correct, but option (c) is not correct.



Reaction (2)

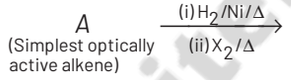
Rate = k[t-ByBr][OH^-], it is a second (base)

order α, β-elimination reaction (E_2), because t-BuBr undergoes dehydrohalogenation (—HBr) with a strong base (alcoholic or ethanolic OH^-) to give an alkene. So, rate of the reaction depends on concentrations of substrate (t-ByBr) and base (OH/alc.). So, option (a) is not correct.

^-OR is a stronger base than ^-OH. So, use of ^-OR will make the E_2 reaction faster.

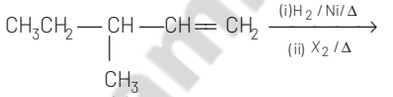
Hence, option (a) is also not correct.

18 The total number of monohalogenated organic products in the following (including stereoisomers) reaction is .....

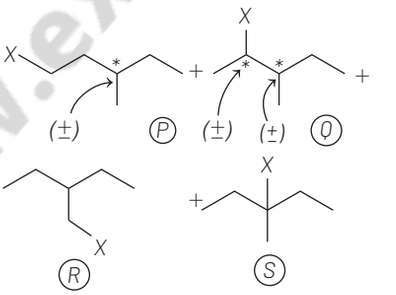


[2020, 3 Sep Shift-I]

Ans. ***(8.00)***



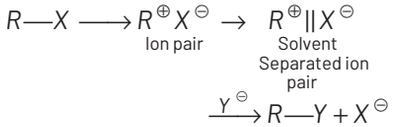
(Simplest optically active alkene)



In the reaction, total number of monohalogenated products (including stereoisomers)

$P = 2$, $Q = 4$, $R = 1$, $S = 1$, i.e. Total = 8

19 The mechanism of S_N1 reaction is given as :



A student writes general characteristics based on the given mechanism as :

(A) The reaction is favoured by weak nucleophiles.

(B) $R^\oplus$ would be easily formed if the substituents are bulky.

(C) The reaction is accompanied by recemisation.

(D) The reaction is favoured by non-polar solvents.

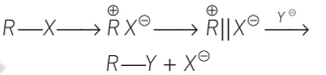
Which observations are correct?

[2020, 3 Sep Shift-I]

(a) (A) and (B) (b) (A) and (C)

(c) (A), (B) and (C) (d) (B) and (D)

Ans. ***(c)***



It indicates $R^\oplus$ (carbocation) formation takes place and $R^\oplus$ got stabilised by electronic factors and polar solvent molecules because solvent separation of $R^\oplus$ is possible.

So, statement (D) is not correct.

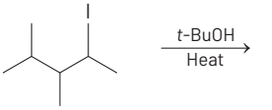
Here, $X^\ominus$ (leaving group) of R—X is substituted by $Y^\ominus$, (nucleophile) *via* the formation of carbocation ($R^\oplus$) intermediate. So, it is an S_N1 reaction.

S_N1 mechanism supports weaker nucleophiles. So, statement (A) is correct.

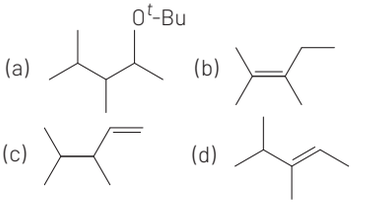
S_N1 reaction is accompanied by inversion and retention in configuration, i.e. racemisation provided 'R' of R—X is chiral. So, statement (C) is correct.

Attachment of bulkier substituents or 3°-nature of the carbon atom of C—X bond of R—X will favour formation of $R^\oplus$ (carbocation). So, statement (B) is also correct.

20 The major product in the following reaction is



[2020, 3 Sep Shift-II]



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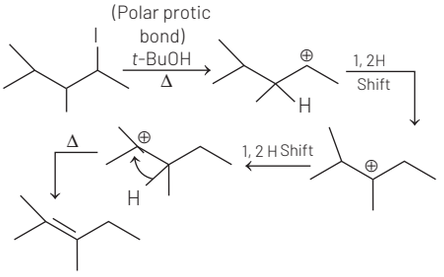
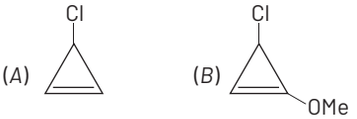
Ans. ***(b)***

Complete reaction is as follows :



The alkene formed is stable according to Saytzeff's rule. It states that alkenes with less number of hydrogen on the double bonded carbon atoms are preffered product.

21 The decreasing order of reactivity of the following organic molecules towards $AgNO_3$ solution is **[2020, 4 Sep Shift-I]**



(C) CH_3CHCH_3 (Cl)

(D) $CH_3CHCH_2NO_2$ (Cl)

(a) (A) > (B) > (C) > (D)
(b) (C) > (D) > (A) > (B)
(c) (B) > (A) > (C) > (D)
(d) (A) > (B) > (D) > (C)

Ans. ***(c)***

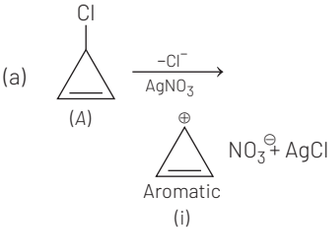
General reaction :

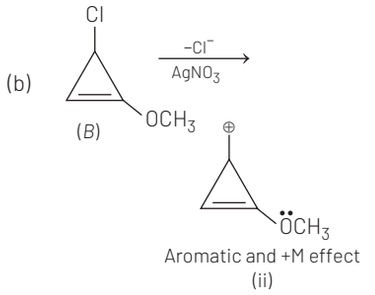
$AgNO_3 + X(\text{Halogen}) \longrightarrow AgX + NO_3^{2-}$

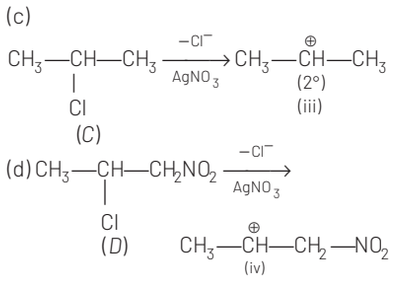
It follows S_N1 reaction.

In S_N1 reaction,

Rate of reaction ∝ stability of carbocation





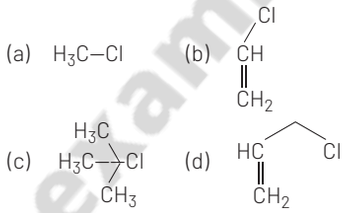


NO_2 shows $-M$ effect

Stability of carbocation is (ii) > (i) > (iii) > (iv).

So, the reactivity order towards $AgNO_3$ solution is (B) > (A) > (C) > (D).

22 Among the following compounds, which one has the shortest C—Cl bond? **[2020, 4 Sep Shift-II]**

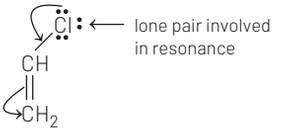


Ans. ***(b)***

In option (c) vinyl chloride, C—Cl bond is shortest due to resonance of lone pair of — Cl (chlorine atom).

Due to resonance C — Cl bond aquire partial double bond character.

Hence, vinyl chloride have least C — Cl bond length.

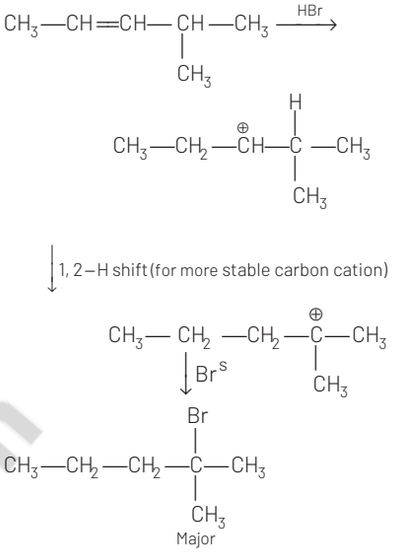


23 The major product formed in the following reaction is

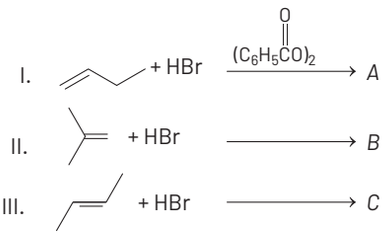
$CH_3CH{=}CHCH(CH_3)_2 \xrightarrow{HBr}$ **[2020, 5 Sep Shift-II]**

(a) $CH_3CH(Br)CH_2CH(CH_3)_2$
(b) $CH_3CH_2CH(Br)CH(CH_3)_2$
(c) $Br(CH_2)_3CH(CH_3)_2$
(d) $CH_3CH_2CH_2C(Br)(CH_3)_2$

Ans. ***(d)***



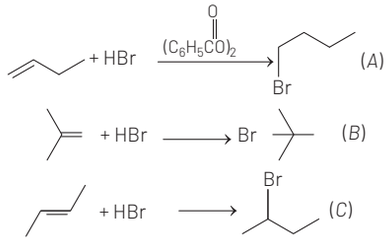
24 The increasing order of the boiling points of the major products *A*, *B* and *C* of the following reactions will be **[2020, 6 Sep Shift-II]**



(a) II < III < I (b) III < I < II
(c) I < II < III (d) I < III < II

Ans. ***(a)***

Complete reaction of I, II and III are as follow:



RX are polar, therefore intermolecular forces of attraction (e.g., dipole-dipole and van der Waals') are stronger in *RX*.

Hence, the boiling point of *RX* is greater than those of hydrocarbons of comparable molecular masses.

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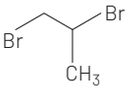
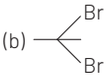
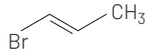
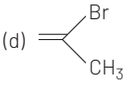
Branching decreases the surface area as in alkane because the branched *C* chains are more spherical -like, which results in lower boiling point.

$$B.P \propto \frac{1}{\text{Branching}}$$

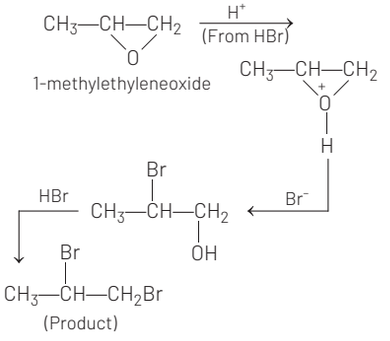
Hence, the boiling point of isomeric *RX* decreases with increase in branching, hence the order will be $B < C < A$.

25 1-methyl ethylene oxide when treated with an excess of HBr produces : **[2020, 7 Jan Shift-I]**

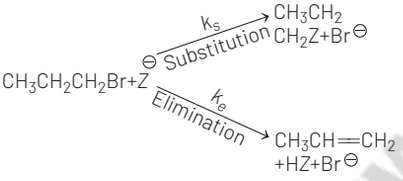
(a) 
(b) 
(c) 
(d) 

Ans. ***(a)***

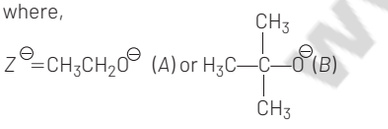
The given reaction is completed as follows :



26 For the following reactions :



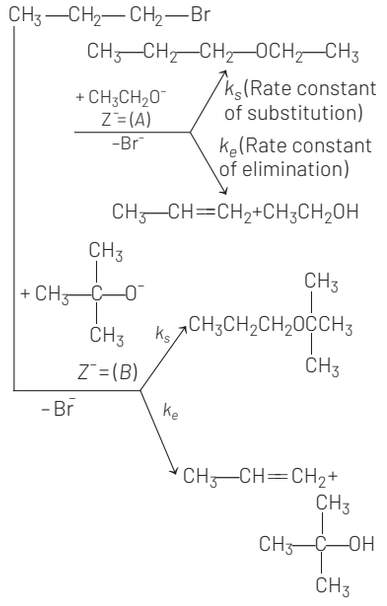
where,



k_s and k_e, are respectively the rate constants for substitution and elimination, and $\mu = \frac{k_s}{k_e}$, the correct option is ..... . **[2020, 7 Jan Shift-II]**

(a) $\mu_B > \mu_A$ and k_e $(B) > k_e$ (A)
(b) $\mu_B > \mu_A$ and k_e $(A) > k_e$ (B)
(c) $\mu_A > \mu_B$ and k_e $(A) > k_e$ (B)
(d) $\mu_A > \mu_B$ and k_e $(B) > k_e$ (A)

Ans. ***(d)***



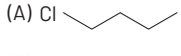
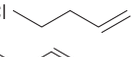
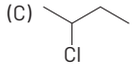
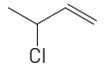
When alkyl halides react with nucleophiles (Z^-), both substitution and elimination reactions can be expected. 1° alkyl halides generally favour substitution, but stronger bases favour elimination. So, in the above reactions in which ($CH_3—CH_2—CH_2—Br$ is 1° alkyl halide, $CH_3CH_2—O^-$ is a strong base), reasonable amounts of substitution and elimination products can form between $A = CH_3CH_2O^-$ and alkyl halide.

(*A*) is an unhindered nucleophile, so it can give substitution better than (*B*) which is hindered (more crowded or sterically hindered). But (*B*) tends to give elimination better than (*A*) due to the same reason also.

$\therefore \quad \mu = \frac{k_s}{k_e}$ is in the order $A > B$

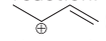
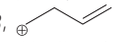
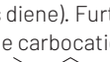
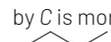
and k_e is in the order $B > A$.

27 The decreasing order of reactivity towards dehydrohalogenation (E_1) reaction of the following compounds is : **[2020, 8 Jan Shift-I]**

(A) 
(B) 
(C) 
(D) 

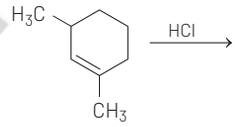
(a) B > A > D > C
(b) B > D > A > C
(c) D > B > C > A
(d) B > D > C > A

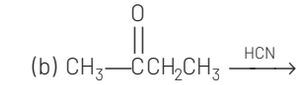
Ans. ***(c)***

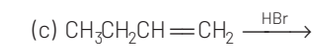
E_1 reaction proceeds *via* carbocation formation, therefore greater the stability of carbocation faster is the reaction. Carbocation formed by *D*,  (2°, resonance stabilised the product is diene) is most stable followed by *B*,  (1° and the product formed is diene). Further among C and *A*, the carbocation formed by *C* is more stable  (2°) than *A*,  (1°). Thus, the reactivity towards dehydrohalogenation follows the order :

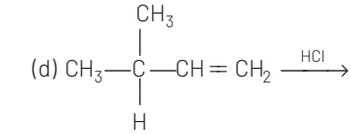
$$D > B > C > A$$

28 Which of the following reactions will not produce a racemic product? **[2020, 9 Jan Shift-II]**

(a) 

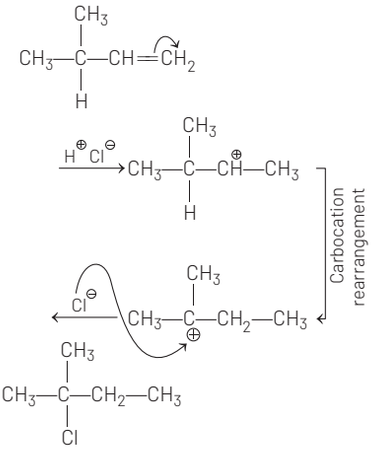
(b) 

(c) 

(d) 

Ans. ***(d)***

Reaction (d) will not produce a racemic product whereas other reactions will form racemic mixture.



There is no chiral carbon atom present in the product.

$\therefore$ Product would not be a racemic mixture.

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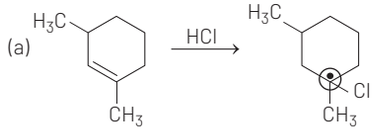
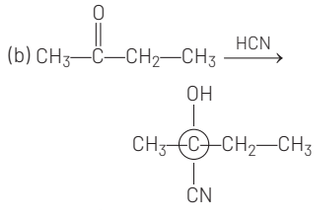
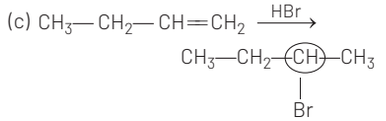
(a) 

Product has a chiral carbon atom (marked by a circle). Both enantiomers are formed in the reaction equally.
∴ It is a racemic mixture.

(b) 

Product has a chiral carbon atom (marked by the circle). Both enantiomers are formed in the reaction equally.
∴ It is a racemic mixture.

(c) 

Product has a chiral carbon atom (marked by the circle). Both enantiomers are formed in equal amount.
∴ It is also a racemic mixture.

29 Which one of the following alkenes when treated with HCl yields majorly an anti Markownikoff product? **[2019, 8 April Shift-II]**

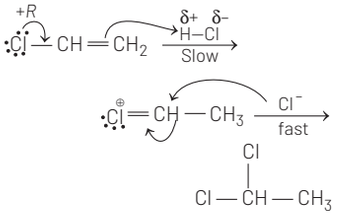
(a) $Cl—CH=CH_2$
(b) $H_2N—CH=CH_2$
(c) $CH_3O—CH=CH_2$
(d) $F_3C—CH=CH_2$

Ans. ***(d)***

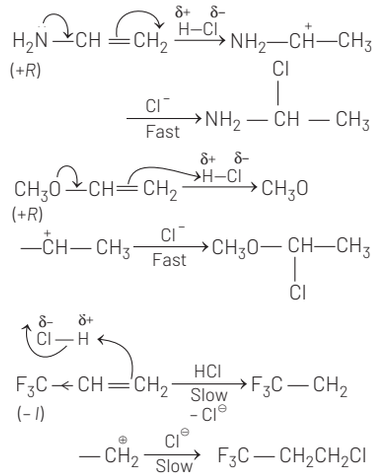
Attachment of electron donating group (+ *R* or + *I*) with sp^2-carbon of an unsymmetrical alkene supports Markownikov's addition rule through electrophilic-addition-pathway.

But, attachment of electron-withdrawing group (– *R* or – *I*) for the same will follow anti-Markownikov's pathway (even in absence of organic peroxide which favours free radical addition) through electrophilic addition pathway.

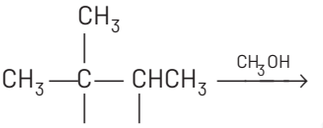
The product formed by given alkenes when treated with HCl.



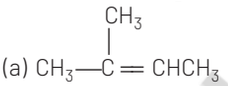
Similarly,

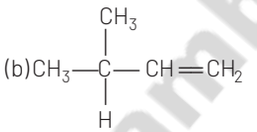


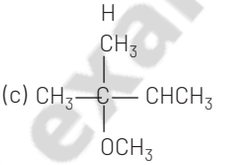
30 The major product of the following reaction is

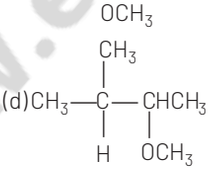


[2019, 10 April Shift-I]

(a) 

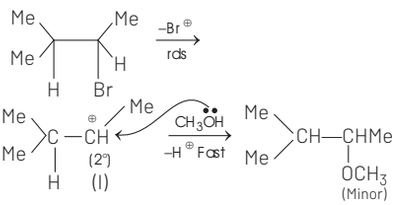
(b) 

(c) 

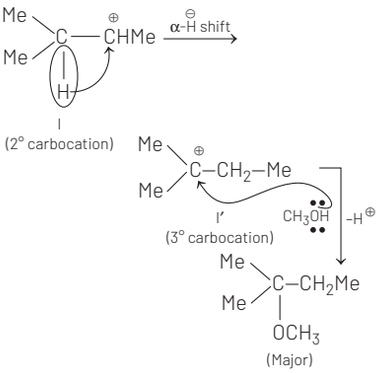
(d) 

Ans. ***(c)***

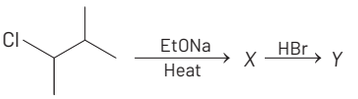
In the given question, the substrate is a 2°-halide (bromide) and the medium, CH_3OH (as well as a poor nucleophile) is protic in nature, So, the reaction will follow mainly S_N1 pathways via the formation of a carbocation intermediate (I).



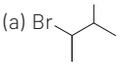
The intermediate, I can be rearranged into the more stable form I′(3°) by α-hydride shift.
I′ will give the major product.

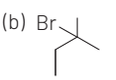


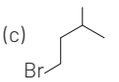
31 The major product *Y* in the following reaction is

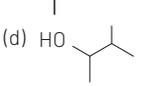


[2019, 10 April Shift-II]

(a) 

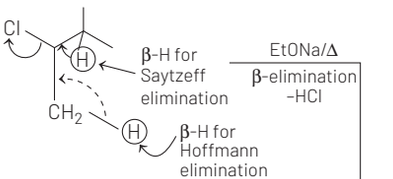
(b) 

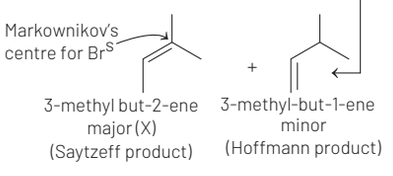
(c) 

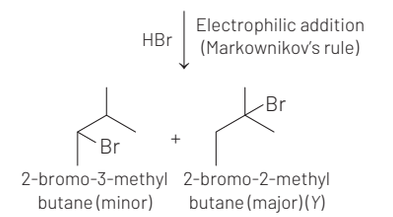
(d) 

Ans. ***(b)***

The given reaction takes place as follows :







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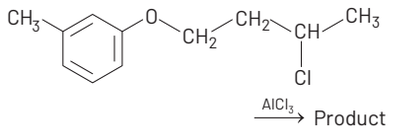
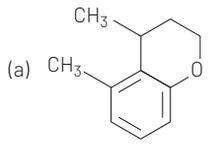
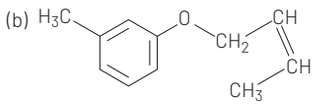
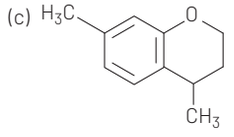
32 The major product obtained in the given reaction is

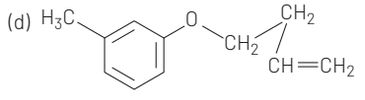


[2019, 10 April Shift II]

(a) 

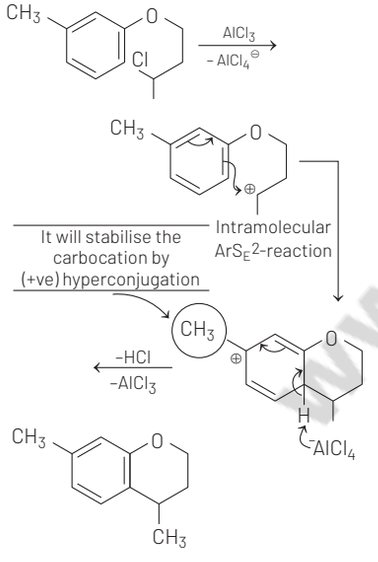
(b) 

(c) 

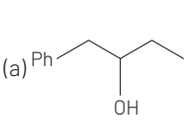
(d) 

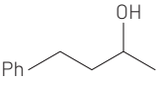
Ans. ***(c)***

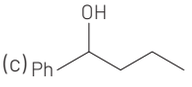
The given reaction takes place as follows :

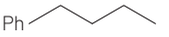


33 Heating of 2-chloro-1-phenyl butane with EtOK/EtOH gives *X* as the major product. Reaction of *X* with $Hg(OAc)_2$ / H_2O followed by $NaBH_4$ gives *Y* as the major product. *Y* is **[2019, 12 April Shift-II]**

(a) 

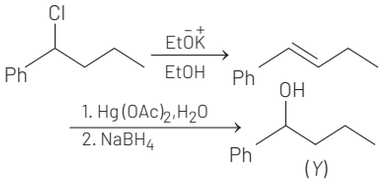
(b) 

(c) 

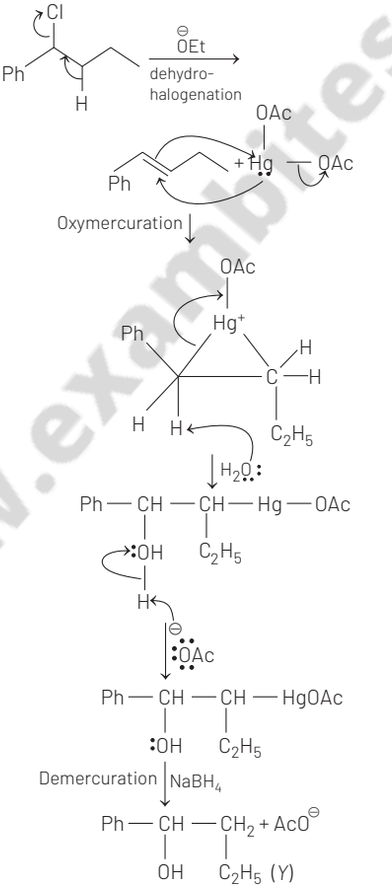
(d) 

Ans. ***(c)***

Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives 1-phenyl but-1-ene(*X*). Reaction of *X* with $Hg(OAc)_2$ / H_2O followed by $NaBH_4$ gives 1-phenyl butan-1-ol (*Y*). Reaction involved is as follows :



Mechanism



34 An Assertion and a Reason are given below. Choose the correct answer from the following options. **[2019, 12 April Shift-II]**

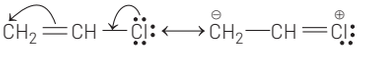
Assertion (A) Vinyl halides do not undergo nucleophilic substitution easily.

Reason (R) Even though the intermediate carbocation is stabilised by loosely held π-electrons, the cleavage is difficult because of strong bonding.

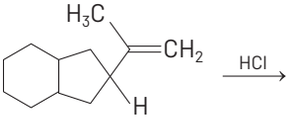
(a) Both (A) and (R) are wrong statements.
(b) Both (A) and (R) are correct statements and (R) is correct explanation of (A).
(c) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).
(d) (A) is a correct statement but (R) is a wrong statement.

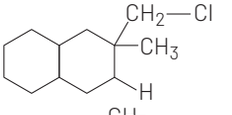
Ans. ***(c)***

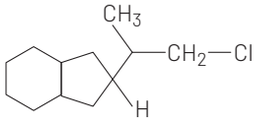
Vinyl halide ($CH_2 = CH—Cl$) do not undergo nucleophilic substitution reactions. This is because it forms highly unstable carbocation ($CH_2 = \overset{\oplus}{C}H$). It cannot delocalise its π-electron. In vinyl halide C—Cl bond possess double bond character also.

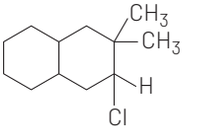


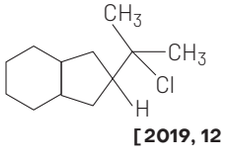
35 The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

[2019, 12 Jan Shift-II]

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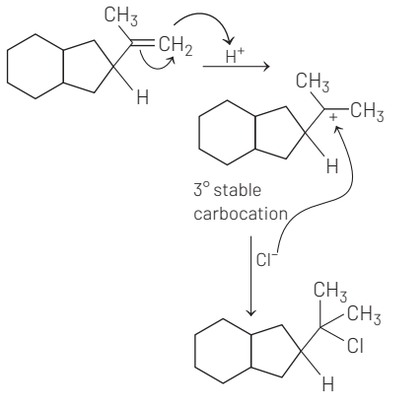
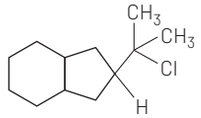
Ans. ***(d)***

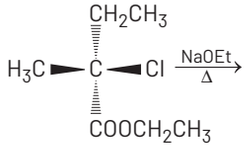
It is a simple case of Markownikoff addition. The reaction proceeds as :



The structure of options given may confuse an aspirant with ring expansion but that is seen as the minor product only [Due to the formation of a 3° stable carbocation in the process] the major product is



36 The major product of the following reaction is **[2019, 12 Jan Shift-II]**



(a) $CH_3CH_2C(=CH_2)CO_2CH_2CH_3$

(b) $CH_3C(CO_2CH_2CH_3)=CHCH_3$

(c) $H_3C-C(CH_2CH_3)(OCH_2CH_3)-COOCH_2CH_3$

(d) $H_3C\,H_2C-C(OCH_2CH_3)(CO_2CH_2CH_3)-CH_3$

Ans. ***(b)***

Presence of strong base (EtO^-) and heat indicates elimination.

Thus, the compound undergo dehydrohalogenation and alkene is produced. As per the position of Cl in substrate, following 2 alkenes are formed as product:

(i) $CH_3CH_2C(=CH_2)COOCH_2CH_3$

(ii) $CH_3CH=C(CH_3)COOCH_2CH_3$

In accordance with Saytzeff rule

$CH_3CH=C(CH_3)COOCH_2CH_3$

will be the major product.

37 Which hydrogen in compound (*E*) is easily replaceable during bromination reaction in presence of light?

$\overset{\delta}{CH_3}-\overset{\gamma}{CH_2}-\overset{\beta}{CH}=\overset{\alpha}{CH_2}$

(*E*)

(a) β-hydrogen (b) δ-hydrogen

(c) γ-hydrogen (d) α-hydrogen

[2019, 10 Jan Shift-I]

Ans. ***(c)***

The compound (*E*) has two allyl-hydrogen atoms (γ). When *E* reacts with $Br_2/h\nu$, it readily undergoes allylic free radical substitution and forms 3, 3-dibromobut-1-ene

$\overset{\delta}{CH_3}-\overset{\gamma}{CH_2}-\overset{\beta}{CH}=\overset{\alpha}{CH_2} \xrightarrow[-HBr]{Br_2/h\nu}$ But-1-ene

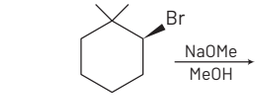
$CH_3-\underset{\gamma}{\underset{|}{CH}}-\underset{\beta}{CH}=\overset{\alpha}{CH_2}$ (Br on γ)

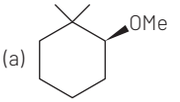
3-bromo-but-1-ene

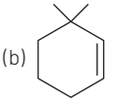
$\xrightarrow[-HBr]{Br_2/h\nu} CH_3-\underset{|}{\overset{Br}{\overset{|}{C}}}-CH=CH_2$ (Br on γ)

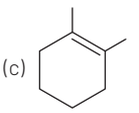
3,3- dibromobut-1-ene

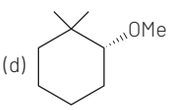
38 The major product of the following reaction is **[JEE Main 2018]**



(a) 

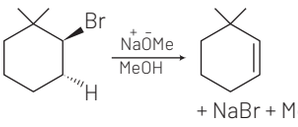
(b) 

(c) 

(d) 

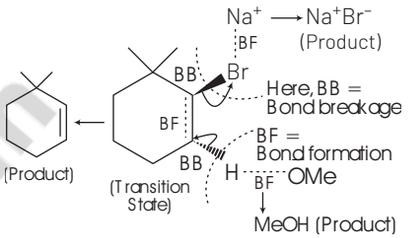
Ans. ***(b)***

Complete reaction can be represented as



Thus, the given reaction is dehydrohalogenation which is a β-elimination proceeding through E_2 mechanism.

Mechanism The reaction proceeds through the formation of following transition state with simultaneous removal of Br and H atoms.



39 The increasing order of reactivity of the following halides for the S_N1 reaction is

I. $CH_3CH(Cl)CH_2CH_3$

II. $CH_3CH_2CH_2Cl$

III. *p*-$H_3CO-C_6H_4-CH_2Cl$

[JEE Main 2017]

(a) (III) < (II) < (I) (b) (II) < (I) < (III)

(c) (I) < (III) < (II) (d) (II) < (III) < (I)

Ans. ***(d)***

(i) The rate of S_N1 reaction depends only upon the concentration of the alkyl halide.

(ii) S_N1 reaction proceeds through the formation of carbocation.

The reactivity is decided by ease of dissociation of alkyl halide.

$R-X \rightleftharpoons R^{\oplus} + X^{\ominus}$

Higher the stability of R^+ (carbocation), higher would be the reactivity towards S_N1 reaction.

p-$H_3CO-C_6H_4-CH_2^{\oplus}$ is the most stable carbocation due to resonance and then $CH_3\overset{\oplus}{C}HCH_2CH_3$ (2° carbocation) while $CH_3CH_2\overset{\oplus}{C}H_2$ (1°) is least stable.

Thus, the correct increasing order of the reactivity of the given halides towards the S_N1 reaction is

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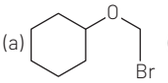
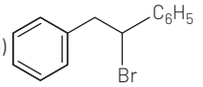
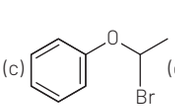
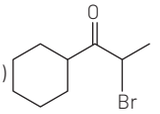
$CH_3CH_2CH_2Cl < CH_3CHCH_2CH_3$ (II), (I) (Cl)

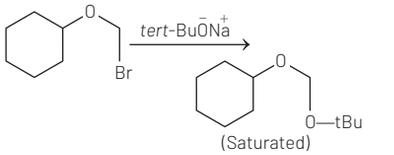
$< p\text{-}CH_3CO-C_6H_4-CH_2Cl$ (III)

40 Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine ? **[JEE Main 2017]**

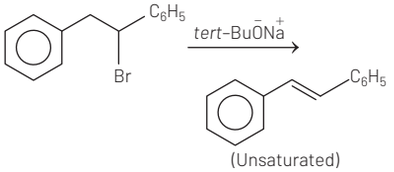
(a) 
(b) 
(c) 
(d) 

Ans. ***(a)***

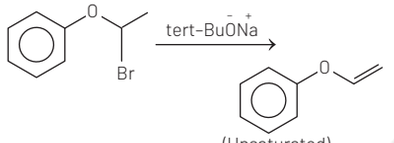
To show decolourisation, compound must be unsaturated.



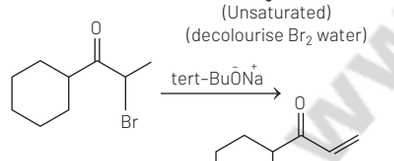
(Saturated)
(cannot decolourise Br_2 water)



(Unsaturated)
(decolourise Br_2 water)



(Unsaturated)
(decolourise Br_2 water)



(Unsaturated)
(decolourise Br_2 water)

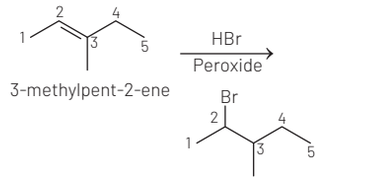
41 3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is **[JEE Main 2017]**

(a) six (b) zero
(c) two (d) four

Ans. ***(d)***

The number of stereoisomers in molecules which are not divisible into two equal halves and have *n* number of asymmetric C-atoms = 2^n.

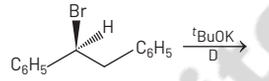
3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product i.e. 2-bromo-3-methyl pentane. It has two chiral centres. Therefore, 4 stereoisomers are possible



3-methylpent-2-ene

Anti-Markownikoff's addition
Four stereoisomers are possible
(As molecule has two chiral centres and asymmetric).

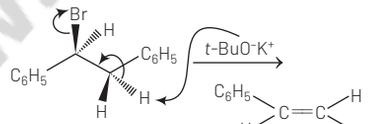
42 The major product obtained in the following reaction is **[JEE Main 2017]**



(a) $(\pm)\,C_6H_5CH(O^tBu)CH_2C_6H_5$
(b) $C_6H_5CH=CHC_6H_5$
(c) $(+)\,C_6H_5CH(O^tBu)CH_2C_6H_5$
(d) $(-)C_6H_5CH(O^tBu)CH_2C_6H_5$

Ans. ***(b)***

An alkyl halide in presence of a bulkier base removes a proton from a carbon adjacent to the carbon bonded to the halogen. This reaction is called E2 (β-elimination reaction).



+ *tert*-BuOH + Br^-

43 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields **[JEE Main 2016]**

I. $C_2H_5CH_2C(CH_3)_2OCH_3$

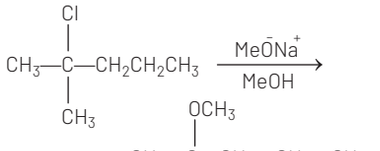
II. $C_2H_5CH_2C(CH_3)=CH_2$

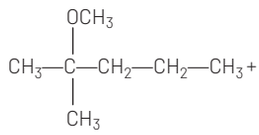
III. $C_2H_5CH=C(CH_3)-CH_3$

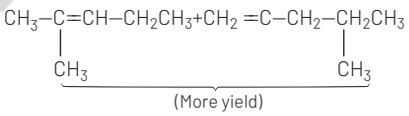
(a) Both I and III
(b) Only III
(c) Both I and II
(d) All of the above

Ans. ***(d)***

Strong nucleophile ($\bar{O}Me$) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.




(Less yield)


(More yield)

44 The synthesis of alkyl fluorides is best accomplished by **[JEE Main 2015]**

(a) free radical fluorination
(b) Sandmeyer's reaction
(c) Finkelstein reaction
(d) Swarts reaction

Ans. ***(d)***

Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. This reaction is known as Swarts reaction.

$$CH_3Br + AgF \longrightarrow \underset{\text{Methyl fluoride}}{CH_3F} + AgBr$$

But, when action of NaI/acetone takes place on alkyl chloride or bromide, alkyl iodide forms. This reaction is called 'Finkelstein reaction'.

$$C_2H_5Cl \xrightarrow[\text{acetone}]{NaI} C_2H_5I + NaCl$$

Free radical fluorination is highly explosive reaction. so not preferred for the preparation of fluoride.

45 How many chiral compounds are possible on monochlorination of 2-methyl butane? **[AIEEE 2012]**

(a) 8 (b) 2 (c) 4 (d) 6

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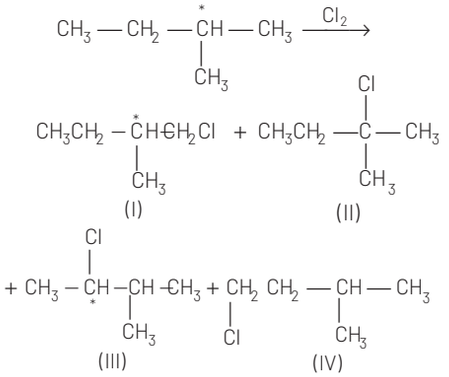
Ans. ***(b)***

2–methylbutane an monochlorination gives 4 isomers, among which I and III are chiral in nature.



Hence, 2 chiral compounds are formed in the above reaction.

46 Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of mono substituted alkyl halide?

[AIEEE 2012]

(a) Tertiary butyl chloride
(b) Neopentane
(c) Isohexane
(d) Neohexane

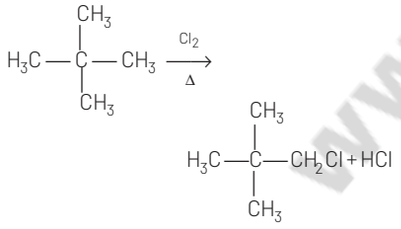
Ans. ***(b)***

Molar mass = 72 = C_nH_{2n+2}
$= 12n + (2n + 2)$
$n = 5$

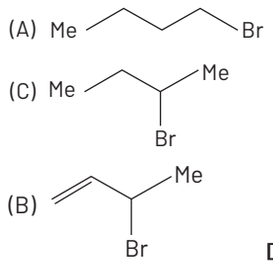
Thus, hydrocarbon is C_5H_{12}.

Since, it gives only single $C_5H_{11}Cl$, This suggests that C_5H_{12} is symmetrical.

Hence, it is containing all 12 equivalent H-atoms.



47 Consider the following bromides,



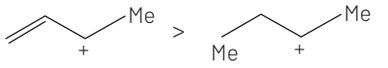
[AIEEE 2010]

The correct order of S_N1 reactivity is

(a) (B)>(C)>(A) (b) (B)>(A)>(C)
(c) (C)>(B)>(A) (d) (A)>(B)>(C)

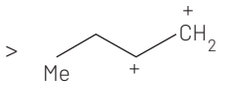
Ans. ***(a)***

The reactivity of S_N1 reaction depends upon the stability of the intermediate, carbocation formed during these reactions. The stabililty order of the carbocation formed from the given species is



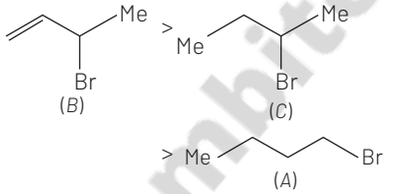
Allylic carbocation (stabilises through resonance due to conjugution)

2°carbocation (stabilises by hyperconjugation due to 6 α-H atoms)



1°carbocation (stablises by hyperconjugation due to 2 α-H-atoms)

Hence, the reactivity order of the given bromide towards S_N1 reaction is



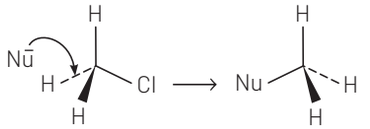
48 The organic chloro compound, which shows complete stereochemical inversion during an S_N2 reaction is

[AIEEE 2008]

(a) $(C_2H_5)_2$ CHCl (b) $(CH_3)_3$ CCl
(c) $(CH_3)_2$CHCl (d) CH_3Cl

Ans. ***(d)***

Nucleophilic substitution bimolecular (S_N2) prefers less sterically hindered site to attack. Lesser the steric hindrance faster the S_N2 reaction. So ease of reaction is 1°>2°>3°.



S_N2 involves inversion of configuration stereo, chemically.

Since, 1° alkyl halides are prone to S_N2 reactions, therefore CH_3Cl undergoes complete strerochemical inversion.

49 Which of the following reactions will yield 2, 2-dibromopropane?

[AIEEE 2007]

(a) $CH_3—C\equiv CH + 2HBr \longrightarrow$
(b) $CH_3CH=CHBr + HBr \longrightarrow$
(c) $CH\equiv CH + 2HBr \longrightarrow$
(d) $CH_3—CH=CH_2 + HBr \longrightarrow$

Ans. ***(d)***

(a) $CH_3—C\equiv CH + HBr \longrightarrow CH_3—\underset{Br}{C}=CH_2$

$\xrightarrow{H^+}$ $\xleftarrow[\text{(Hydride transfer)}]{\text{Rearrangement}}$ $H_3C—\underset{Br}{CH}—\overset{+}{C}H_2$

$\xrightarrow{Br^-}$ $CH_3—\underset{Br}{\overset{Br}{C}}—CH_3$ (2, 2-dibromopropane) ← $CH_3—\underset{Br}{\overset{+}{C}}—CH_3$ (More stable carbocation)

(b) $CH_3CH=CHBr \xrightarrow{HBr} CH_3CH_2CHBr_2$

(c) $CH\equiv CH \xrightarrow{2\,HBr} CH_3CHBr_2$

(d) $CH_3—CH=CH_2 \xrightarrow{HBr} CH_3CHBrCH_3$

50 HBr reacts with $CH_2=CH—OCH_3$ under anhydrous conditions at room temperature to give

(a) CH_3CHO and CH_3Br **[AIEEE 2006]**
(b) $BrCH_2CHO$ and CH_3OH
(c) $BrCH_2—CH_2—OCH_3$
(d) $H_3C—CHBr—OCH_3$

Ans. ***(d)***

$CH_2=CH—OCH_3 \xrightarrow{HBr}$ $CH_3—\underset{Br}{CH}—OCH_3$

First protonation occurs, two possible intermediates are

$\overset{+}{C}H_3 \rightarrow CH \rightarrow OCH_3$ (I)
H

(–*I* effect destabilises carbocation)

and $CH_3—\overset{+}{C}H—O—CH_3$ (II)

(+ *M* effect stabilises carbocation)

II, is more favourable. Hence, $Br^{\ominus}$ attacks and product is

$CH_3—\underset{Br}{CH}—O—CH_3$

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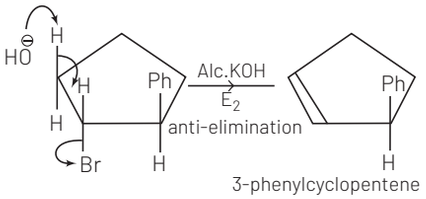
51 *trans*-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces **[AIEEE 2006]**

(a) 4-phenylcyclopentene
(b) 2-phenylcyclopentene
(c) 1-phenylcyclopentene
(d) 3-phenylcyclopentene

Ans. ***(b)***



3-phenylcyclopentene

Anti-elimination, means —H and the —Br both departing group must be present at dihedral angle of 180° (anti).

52 $CH_3Br + Nu^- \longrightarrow CH_3—Nu + Br^-$

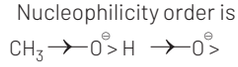
The decreasing order of the rate of the above reaction with nucleophile (Nu^-) *A* and *D* is

[Nu = (*A*) PhO^-, (*B*) AcO^-, (*C*) HO^-, (*D*) CH_3O^-] **[AIEEE 2006]**

(a) D > C > A > B (b) D > C > B > A
(c) A > B > C > D (d) B > D > C > A

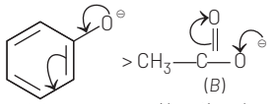
Ans. ***(a)***

Nucleophilicity order is



(*D*) (*C*)

+ *I* effect



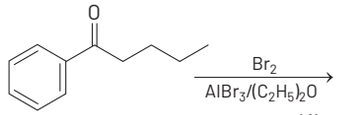
(*A*) (*B*)

Negative charge stabilised by resonance

Negative charge comparatively stable than phenoxide ion

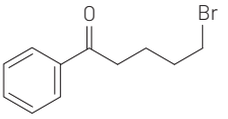
TOPIC 2
Haloarenes

53



'A'
(Major product)

Consider the given reaction, the product *A* is **[2021, 26 Aug Shift-II]**

(a)


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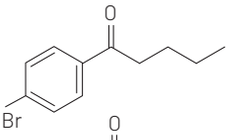
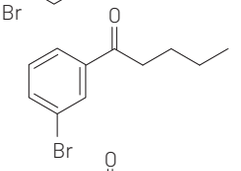
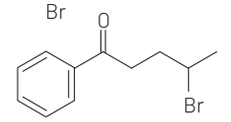
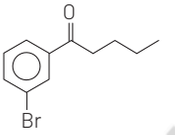


(c)


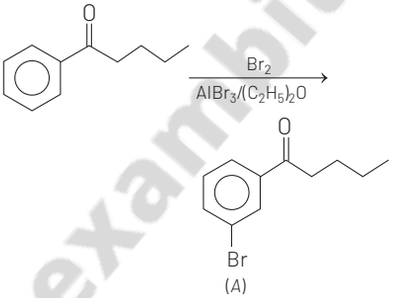
(d)


Ans. ***(c)***

In presence of Lewis acid, electrophilic halogenation reaction takes place at *meta* position to give



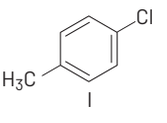
as follows



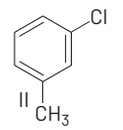
(*A*)
(Major product)

54 Among the following compounds I-IV, which one forms a yellow precipitate on reacting sequentially with

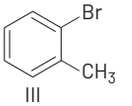
(i) NaOH (ii) dil. HNO_3
(iii) $AgNO_3$? **[2021, 26 Aug Shift-I]**



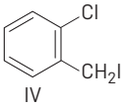
I



II



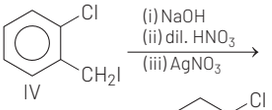
III



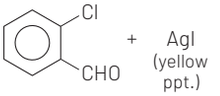
IV

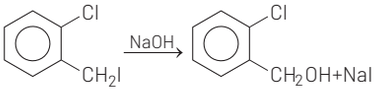
(a) II (b) IV (c) I (d) III

Ans. ***(b)***

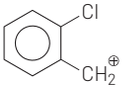


IV





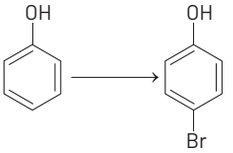
This compound halide will only give yellow ppt. as benzyl carbocation formed shown below is highly stable by conjugation.



Benzyl carbocation

Other compounds halide cannot be removed because their corresponding carbocation is highly unstable.

55



(Major product)

The given reaction can occur in the presence of

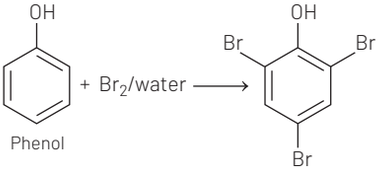
(A) bromine water
(B) Br_2 in CS_2, 273 K
(C) Br_2 / $FeBr_3$
(D) Br_2 in $CHCl_3$, 273 K

Choose the correct answer from the options given below **[2021, 22 July Shift-I]**

(a) (B) and (D) only
(b) (A) and (C) only
(c) (B), (C) and (D) only
(d) (A), (B) and (D) only

Ans. ***(c)***

Only bromine water gives tribromo products, while all other gives monobromo products in which *para* bromo is major product.



Phenol

2,4,6-tribromophenol
(Major product)

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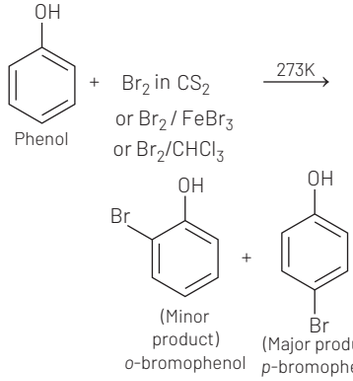
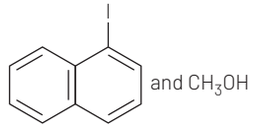
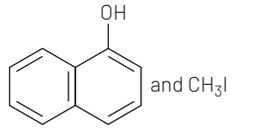
When phenol reacts with bromine in the presence of CS_2, $FeBr_3$, $CHCl_3$0, it results in the formation of two products. The products is *ortho* bromophenol and *para* bromophenol. The major product of this reaction is *p*-bromophenol because no steric hindrance is present at *para* position.

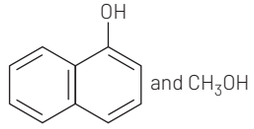


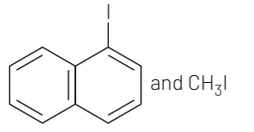
56 Main products formed during a reaction of 1-methoxy naphthalene with hydroiodic acid are

[2021, 18 March Shift-II]

(a)  and CH_3OH

(b)  and CH_3I

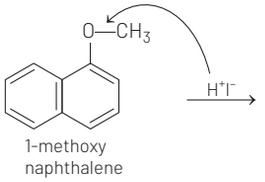
(c)  and CH_3OH

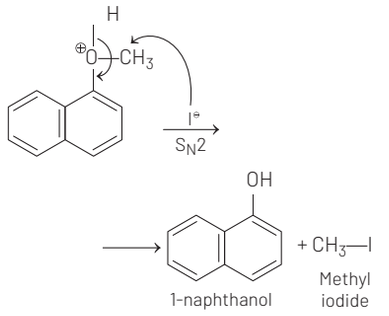
(d)  and CH_3I

Ans. ***(b)***

Given reaction is completed *via* S_N2 mechanism. Methyl of methoxy group will be substituted by H^+ ion to give —OH(hydroxy group) as follows

Mechanism





57 Which of the following reaction is an example of ammonolysis?

[2021, 17 March Shift-I]

(a) $C_6H_5COCl + C_6H_5NH_2 \longrightarrow C_6H_5CONHC_6H_5$

(b) $C_6H_5CH_2CN \xrightarrow{[H]} C_6H_5CH_2CH_2NH_2$

(c) $C_6H_5NH_2 \xrightarrow{HCl} C_6H_5\overset{+}{N}H_3Cl^-$

(d) $C_6H_5CH_2Cl + NH_3 \longrightarrow C_6H_5CH_2NH_2$

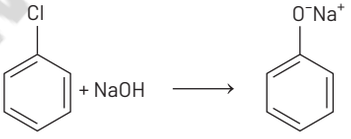
Ans. ***(d)***

Reaction of alkyl halide with ammonia is called ammonolysis reaction.

$$C_6H_5CH_2Cl \xrightarrow{NH_3} C_6H_5CH_2NH_2$$

Carbon-halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile. Hence, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (—NH_2) group.

This process of cleavage of the C—*X* bond by ammonia molecule is known as ammonolysis.

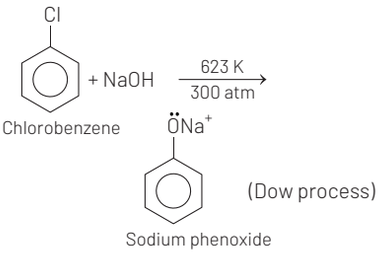
58 

The above reaction requires which of the following reaction conditions? **[2021, 17 March Shift-I]**

(a) 573 K, Cu, 300 atm
(b) 623 K, Cu, 300 atm
(c) 573 K, 300 atm
(d) 623 K, 300 atm

Ans. ***(d)***

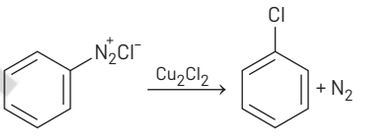
When chlorobenzene is treated with NaOH at 623 K and 300 atm sodium phenoxide is formed by nucleophilic substitution.

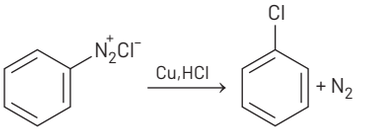


Nucleophilic substitution is not preferred in aromatic compounds. So, to do such reactions high temperature and pressure are required.

59 Match List-I with List-II.

List-I

A. 

B. 

C. $2CH_3CH_2Cl + 2Na \xrightarrow{Ether} C_2H_5—C_2H_5 + 2NaCl$

D. $2C_6H_5Cl + 2Na \xrightarrow{Ether} C_6H_5—C_6H_5 + 2NaCl$

List-II

(i) Wurtz reaction
(ii) Sandmeyer reaction
(iii) Fittig reaction
(iv) Gattermann reaction

Choose the correct answer from the options given below.

[2021, 26 Feb Shift-II]

	A	B	C	D
(a)	(iii)	(i)	(iv)	(ii)
(b)	(ii)	(i)	(iv)	(iii)
(c)	(ii)	(iv)	(i)	(iii)
(d)	(iii)	(iv)	(i)	(ii)

Ans. ***(c)***

Benzene diazonium chloride undergoes Sandmeyer reaction in presence of Cu_2Cl_2 while undergoes Gattermann reaction in presence of Cu/HCl to give chlorobenzene along with nitrogen gas (N_2).

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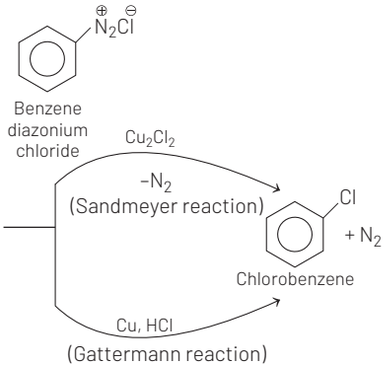


So, (A) - (ii) Sandmeyer reaction

(B) - (iv) Gattermann reaction

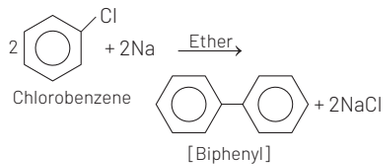
(C) Ethyl chloride reacts with sodium in presence of dry ether to give *n*-butane. This reaction is known as Wurtz reaction.

$$\underset{\text{Ethyl chloride}}{2CH_3CH_2Cl} + 2Na \xrightarrow{\text{Ether}} \underset{n\text{-butane}}{CH_3CH_2{-}CH_2CH_3} + 2NaCl$$

[Aliphatic 1°-halide]

It is Wurtz reaction in which an aliphatic 1° or 2° halides produces a symmetrical alkane like *n*-butane.

(D) Chlorobenzene reacts with sodium in presence of dry ether to give biphenyl. This is known as Fittig reaction.



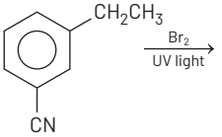
It is Fittig reaction in which a halobenzene produces biphenyl.

So, C - (i) Wurtz reaction

D - (iii) Fittig reaction

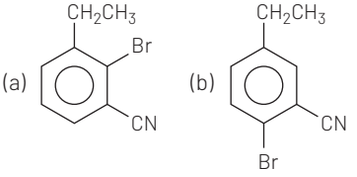
So, correct match is A-(ii), B-(iv), C-(i) and D-(iii).

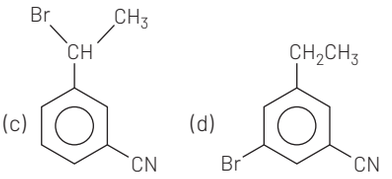
60 For the given reaction,



A
(Major product)
monobrominated

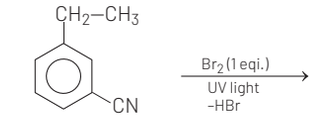
What is *A*? **[2021, 26 Feb Shift-I]**



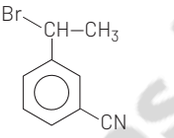


Ans. ***(c)***

When 3-ethyl benzonitrile undergoes photochemical reaction (UV) with bromine (1 equivalent), we get a monobrominated product 1 bromo -1(3 - cyanophenyl) ethane (*A*) as the major product.



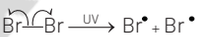
3-ethyl benzonitrile



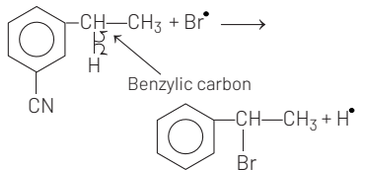
(*A*)
1-bromo-1(3-cyanophenyl) ethane (Major)

The reaction follows benzylic free radical substitution mechanism which has a 2° benzylic free radical intermediate (stable due to resonance with the benzene ring).

(i) Initiation step In this step radicals are generated *via* homolytic fission of covalent bond.

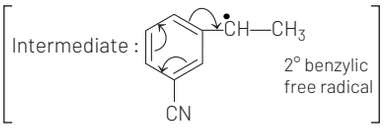


(ii) Propagation step 3-methyl benzonitrile reacts with bromine radical to give 1-bromo-1-(3-cyanophenyl) ethane along with $H^\bullet$.

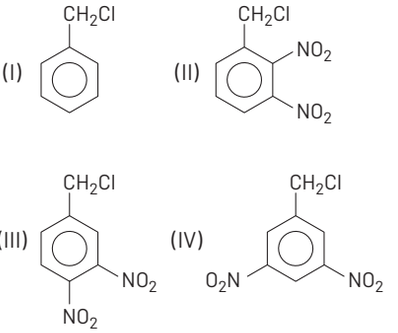


(iii) Termination step $H^\bullet$ and $Br^\bullet$ reacts to form HBr.

$H^\bullet + Br^\bullet \longrightarrow HBr$



61 The decreasing order of reactivity of the following compounds towards nucleophilic substitution (S_N2) is



[2020, 3 Sep Shift-II]

(a) (II) > (III) > (IV) > (I)
(b) (IV) > (II) > (III) > (I)
(c) (III) > (II) > (IV) > (I)
(d) (II) > (III) > (I) > (IV)

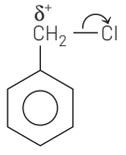
Ans. ***(a)***

Rate of S_N2 reaction

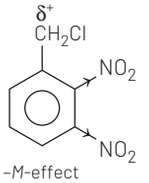
$$\propto \frac{1}{\text{Stability of carbocation}}$$

$$\text{Stability of carbocation} \propto \frac{1}{-I/-M}$$

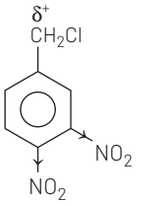
(effective group)



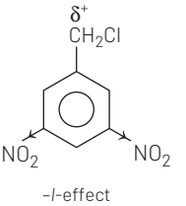
-*I*-effect
(I)



-*M*-effect
-*I*-effect
(II)
(Distance dominating)



-*M*-effect
-*I*-effect
(III)



-*I*-effect
(IV)

So, the decreasing order of reactivity of the given compounds toward S_N2 reaction is

(II) > (III) > (IV) > (I).

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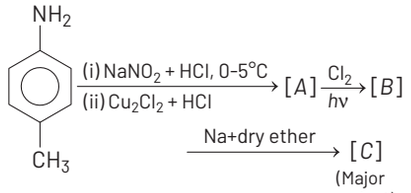
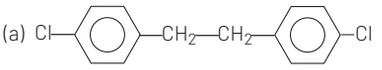
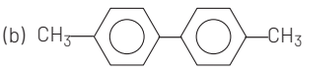
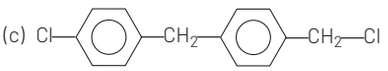
62 In the following reaction sequence, [*C*] is

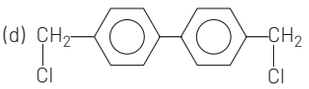


[2020, 4 Sep Shift-II]

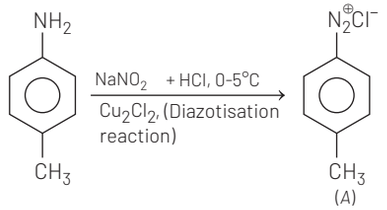
(a) 

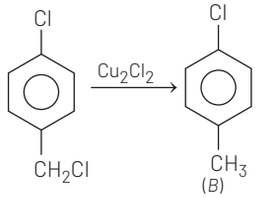
(b) 

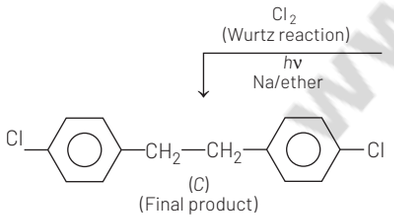
(c) 

(d) 

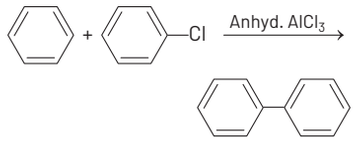
Ans. ***(a)***

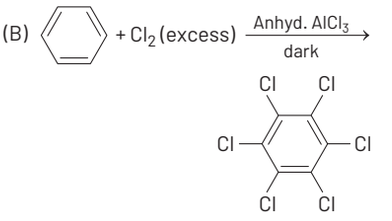


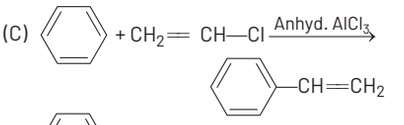


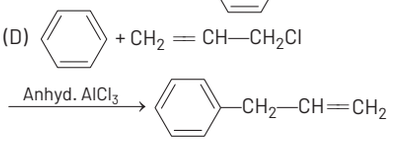


63 Consider the following reactions :

(A) 

(B) 

(C) 

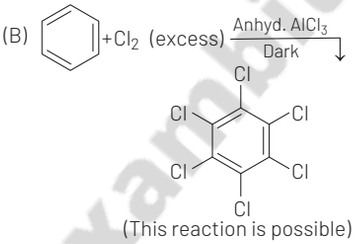
(D) 

Which of these reactions are possible? **[2020, 7 Jan Shift-II]**

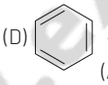
(a) (B) and (D) (b) (A) and (D)
(c) (B), (C) and (D) (d) (A) and (B)

Ans. ***(a)***

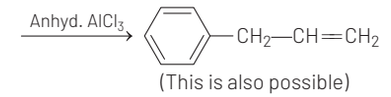
(A) and (C) are not possible : Aryl halides and vinyl halides in the presence of anhyd. $AlCl_3$ do not act as electrophiles to give Friedel-Crafts reaction with benzene. Therefore, these reactions are not possible.

(B) 

(This reaction is possible)

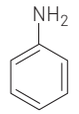
(D)  + CH_2=CH—CH_2—Cl

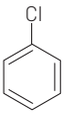
(Allyl halide : easily form electrophile with $AlCl_3$ and can react with benzene to give Friedel-Craft's reaction)

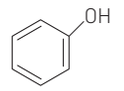


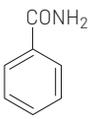
(This is also possible)

64 Which of these will produce the highest yield in Friedel-Crafts reaction? **[2020, 9 Jan Shift-I]**

(a) 

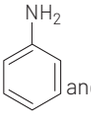
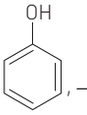
(b) 

(c) 

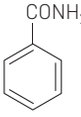
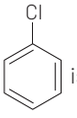
(d) 

Ans. ***(b)***

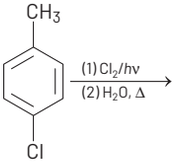
Friedel-Crafts reaction is an electrophilic substitution reaction. In general, the rate of these reactions is highest when benzene have some electron releasing groups, (i.e. —NH_2, —OH) attached to the nucleus.

But in  and  , —$\ddot{N}H_2$ and —$\ddot{O}H$ groups are deactivated because the Lewis acid (anhydrous $AlCl_3$) used in these reactions form an adduct with the '—NH_2' or —OH' groups and becomes ineffective.

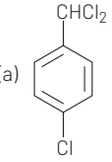
' ' is a electron withdrawing (deactivating) group.

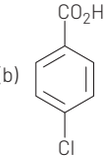
∴  is not highly reactive. '—Cl' in  is weakly electron withdrawing (deactivating) group, but among the given options, it is most reactive towards Friedel-Crafts reaction.

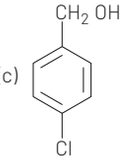
65 The major product of the following reaction is

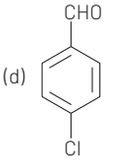


[2019, 8 April Shift-II]

(a) 

(b) 

(c) 

(d) 

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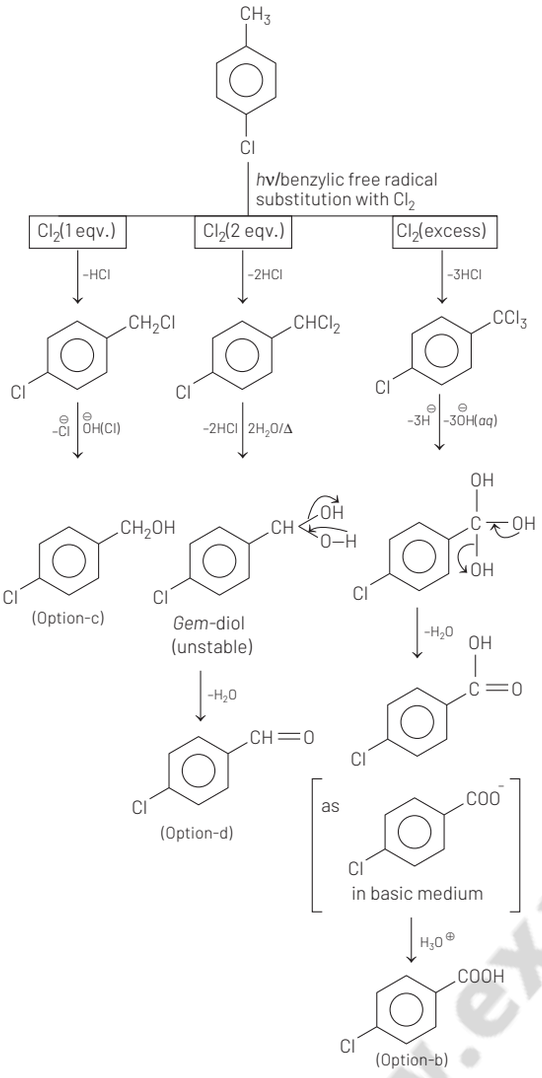
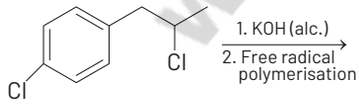
Ans. ***(d)***

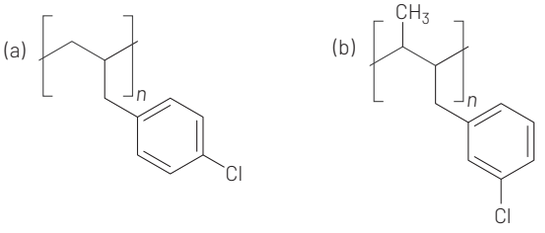


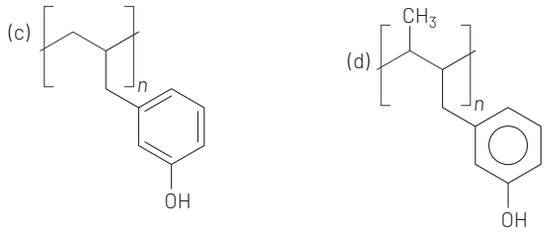
So, considering the second reaction condition, Cl^-, H_2O, Δ in the statement of the question, the correct answer is option (d).

66 The major product of the following reaction is



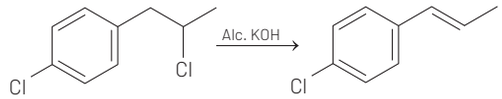
[2019, 9 April Shift-I]



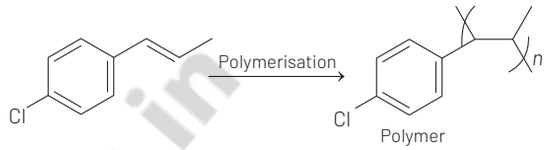


Ans. ***(b)***

In presence of alc. KOH, the given halide undergoes elimination reaction.

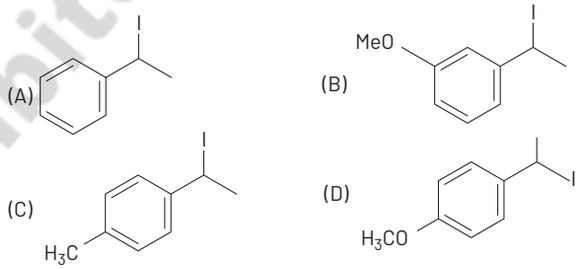


The alkene produced undergoes polymerisation *via* free radical mechanism. This process involve three steps, i.e. initiation, propagation and termination.



67 Increasing rate of S_N1 reaction in the following compounds is

[2019, 10 April Shift-I]

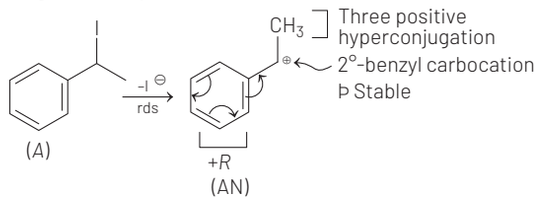


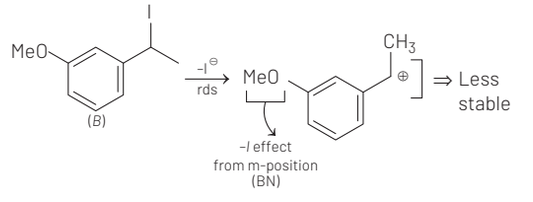
(a) (A) < (B) < (C) < (D)
(b) (B) < (A) < (C) < (D)
(c) (A) < (B) < (D) < (C)
(d) (B) < (A) < (D) < (C)

Ans. ***(b)***

More stable the carbocation intermediate, higher will be the rate of S_N1 reaction.

The reaction involving carbocation intermediate formation for the given compounds are as follows:





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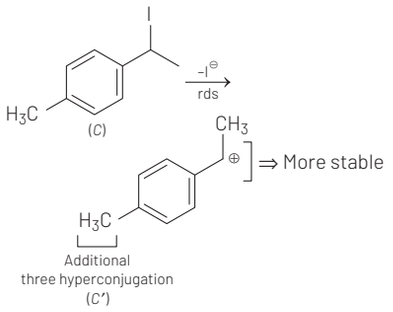
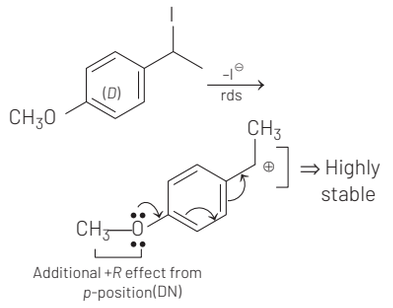


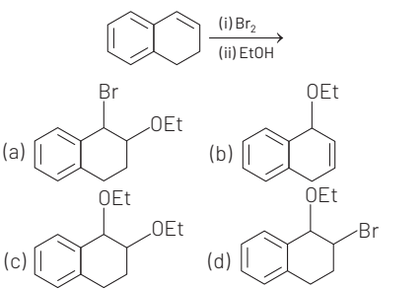


Stability of intermediates will follow the order

$$\underset{(-I)}{B'} < \underset{(-HPC=3)}{A'} < \underset{(+HPC=6)}{C'} < \underset{\substack{(+HPC=3\\+R=1)}}{D'}$$

So, the rate of S_N1 reaction with the given compounds will be, $B < A < C < D$

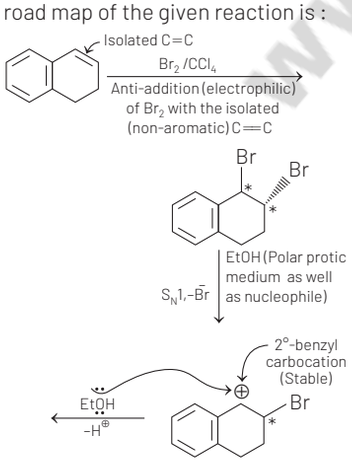
68 The major product of the following reaction is

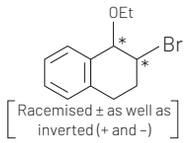


[2019, 9 Jan Shift-I]

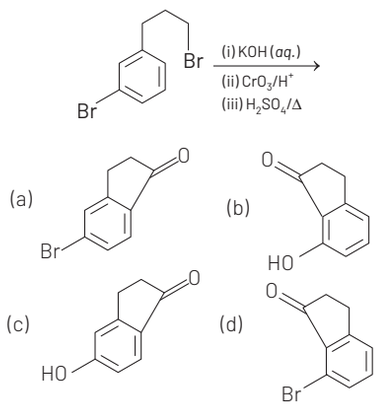
Ans. ***(d)***

The road map of the given reaction is :





69 The major product of the following reaction is

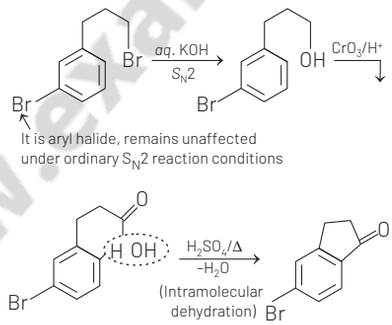


[2019, 9 Jan Shift-I]

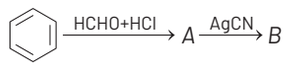
Ans. ***(a)***

Key Idea The reaction involves hydrolysis or nucleophilic substitution in first step followed by oxidation and dehydration in last step. The most important fact is that, the Br group attached directly to aromatic ring will not undergo substitution in step (i)

The road map of the given reaction is as follows:



70 The compounds *A* and *B* in the following reaction are, respectively



(a) *A* = Benzyl alcohol,
B = Benzyl isocyanide

(b) *A* = Benzyl alcohol,
B = Benzyl cyanide

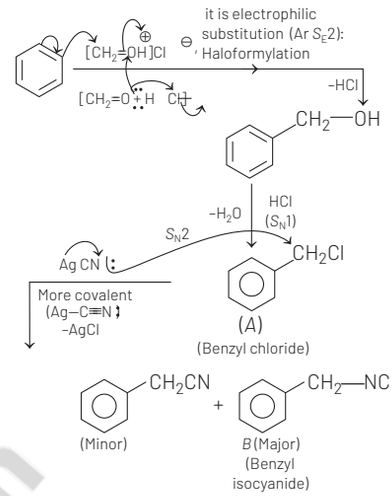
(c) *A* = Benzyl chloride,
B = Benzyl isocyanide

(d) *A* = Benzyl chloride,
B = Benzyl cyanide

[2019, 9 Jan Shift-I]

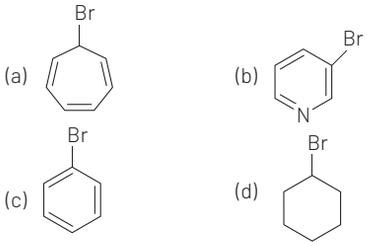
Ans. ***(c)***

The mechanism of the given reaction is as follows:



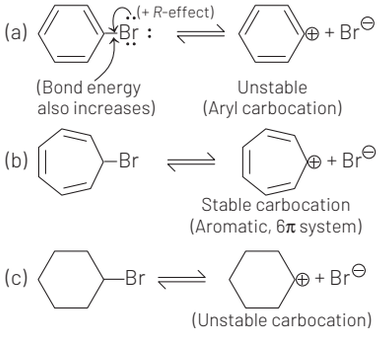
Thus, both benzyl cyanide and benzyl isocyanide are the products of reaction but benzyl isocyanide being the major product gives the correct option as (c).

71 Which of the following compounds will produce a precipitate with $AgNO_3$? **[2019, 11 Jan Shift-II]**



Ans. ***(a)***

Only ionic halides (X^-) give precipitate of AgX with $AgNO_3$ solution. So, an organic bromide able to produce $R^{\oplus}$ (stable carbocation) and Br^- in aqueous solution will give precipitate of AgBr with $AgNO_3$.



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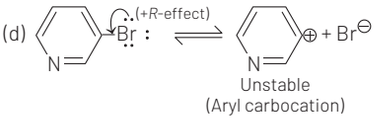
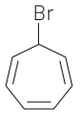
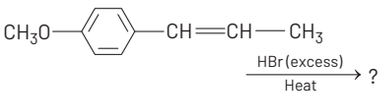
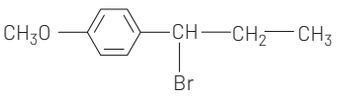
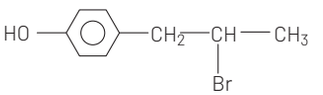
(d) 

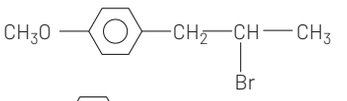
So, only  produces a precipitate of AgBr with $AgNO_3$ solution.

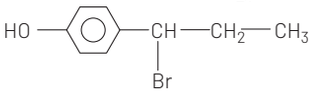
72 The major product in the following conversion is **[2019, 12 Jan Shift-II]**



(a) 

(b) 

(c) 

(d) 

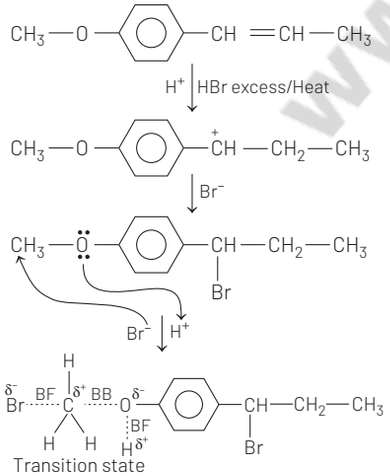
Ans. ***(d)***

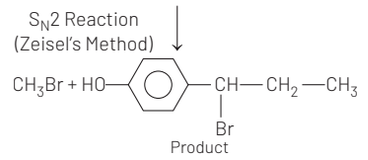
Key Idea The excess of HBr and high temperature in given reaction serves for dual purpose :

(i) Hydrolysis of ether *via* S_N2 mechanism, i.e. Zeisel's method.

(ii) Markownikoff addition at double bond of the branch.

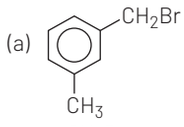
The road map of complete reaction is as follows:

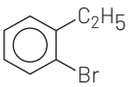


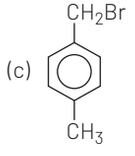


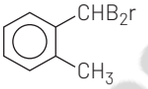
Here, BB = Bond breakage
BF = Bond formation

73 Compound (*A*), C_8H_9Br gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (*A*) gives an acid (*B*), $C_8H_6O_4$. (*B*) easily forms anyhydride on heating. Identify the compound (*A*). **[JEE Main 2013]**

(a) 

(b) 

(c) 

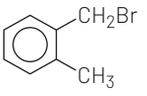
(d) 

Ans. ***(d)***

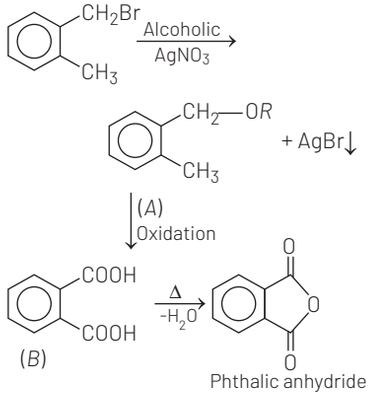
Compound *A* gives a precipitate with alcoholic $AgNO_3$ (here white is misprinting because the colour of ppt is light yellow), so it must contains Br in side chain. On oxidation, it gives $C_8H_6O_4$, which shows the presence of two alkyl chains attached directly with the benzene nucleus.

Since, compound *B* gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) position.

Thus, *A* must be



and the reactions are as follows

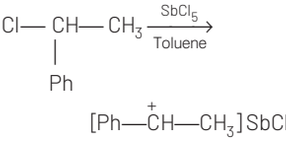


74 A solution of (–*l*)-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of **[JEE Main 2013]**

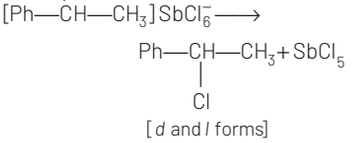
(a) carbanion (b) carbene
(c) carbocation (d) free radical

Ans. ***(c)***

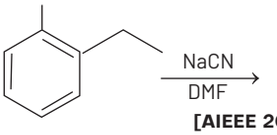
The given compound, (–*l*)–chloro-1-phenylethane in the presence of $SbCl_5$ forms a carbocation.



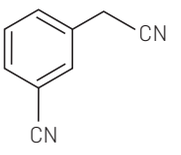
Since, the carbocation is a planar species, therefore it can be attacked by $SbCl_6^-$ either from the front or back side of the carbocation with equal ease. As a result, 50 : 50 mixture of two enantiomers of 1–chloro–1–pheynylethane undergoes racemization due to the formation of a carbocation intermediate.

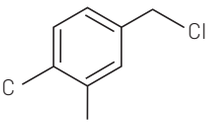


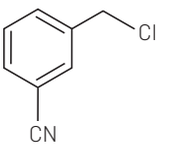
75 The structure of the major product formed in the following reaction is

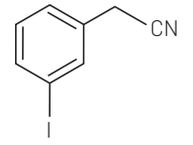


[AIEEE 2006]

(a) 

(b) 

(c) 

(d) 

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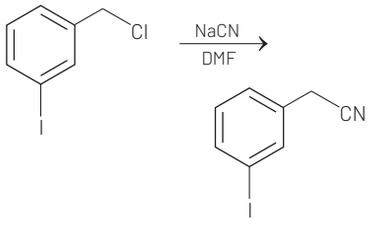
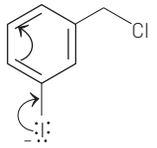
Ans. ***(d)***



Chloride present on 1° aliphatic carbon can be substituted easier than iodide because I is attached to benzene ring. Lone pair of e^- of I is involved in delocalisation with $\pi - e^-$ of benzene.

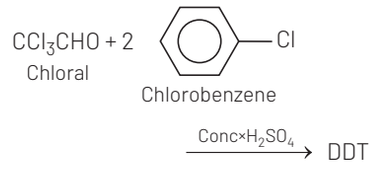


Hence, I is difficult to substitue.

76 The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is **[AIEEE 2004]**

(a) gammexane
(b) DDT
(c) freon
(d) hexachloroethane

Ans. ***(b)***



77 Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled *A* and *B* for testing . *A* and *B* were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance *B* gave a yellow precipitate. Which one of the following statements is true for this experiment? **[AIEEE 2003]**

(a) *A* was C_6H_5I
(b) *A* was $C_6H_5CH_2I$
(c) *B* was C_6H_5I
(d) Addition of HNO_3 was unnecessary

Ans. ***(a)***

In tube A

$$C_6H_5I \xrightarrow[\text{boil}]{NaOH} \text{No reaction } (\because \text{pH} - I \text{ does not break})$$

$$\xrightarrow[(ii)\ AgNO_3]{(i)\ \text{Dil. } HNO_3} \underset{\text{yellow ppt. of AgI}}{\text{No}}$$

In tube B

$$C_6H_5CH_2I \xrightarrow[-C_6H_5CH_2OH]{NaOH,\ \text{boil}} NaI \xrightarrow[(ii)\ AgNO_3]{(i)\ \text{Dil. } HNO_3} \underset{\text{yellow ppt.}}{AgI}$$

$(PhCH_2I \text{ bonds breaks})$

Thus, *A* was C_6H_5I.

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25

Organic Compounds Containing Oxygen

TOPIC 1
Alcohols and Phenols

01 Given below are two statements.
One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Treatment of bromine water with propene yields 1-bromopropan-2-ol.

Reason (R) Attack of water on bromonium ion follows Markownikoff rule and results in 1-bromopropan-2-ol.

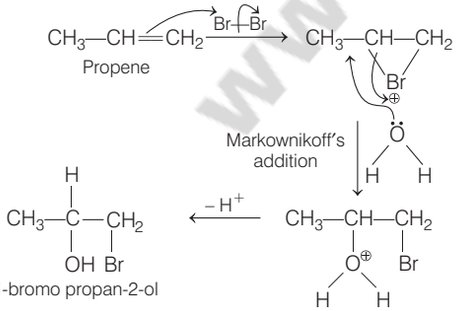
In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 31 Aug Shift-I]

(a) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(b) (A) is false but (R) is true.
(c) Both (A) and (R) are true and (R) is the correct explanation of (A).
(d) (A) is true but (R) is false

Ans. ***(c)***

Propene reacts with bromine water to yield 1-bromopropan-2-ol.

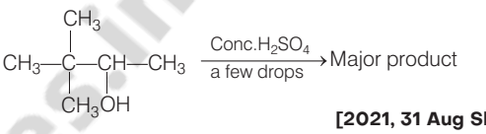


Markownikoff's rule states that in an unsymmetrical alkene the electron rich nucleophile adds to the C-atom with lesser number of hydrogen.

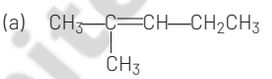
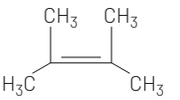
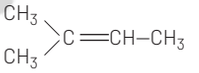
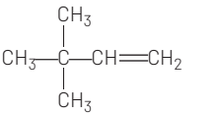
Hence, both A and R are true and R is the correct explanation of A.

Hence, correct option is (c).

02 The major product formed in the following reaction is

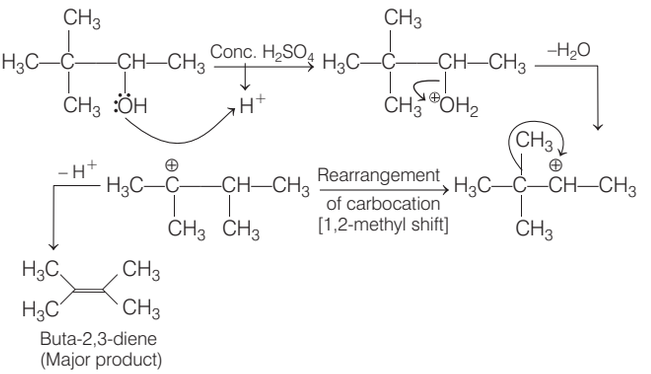


[2021, 31 Aug Shift-I]

(a) 
(b) 
(c) 
(d) 

Ans. ***(b)***

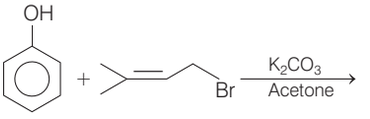
3,3-dimethylbutan-2-ol reacts with concentrated H_2SO_4 to form but-2,3-diene.



Hence, correct option is (b).

03 The major product of the following reaction, if it occurs by S_N2 mechanism is

[2021, 27 Aug Shift-II]



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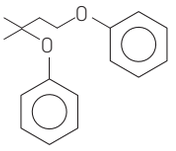
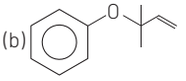
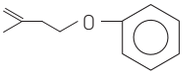
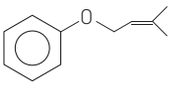
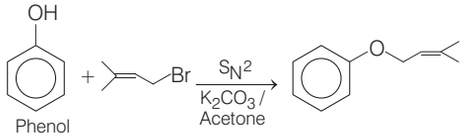
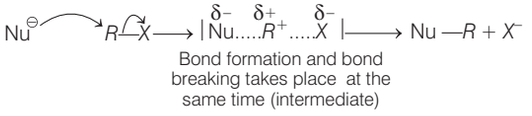
(a) 
(b) 
(c) 
(d) 

Ans. ***(d)***

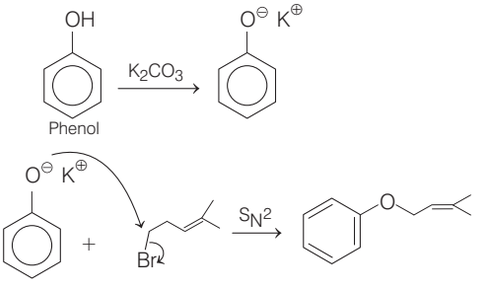
In S_N2 reaction, no formation of carbocation takes place. The nucleophile here which is phenoxide attacks from the back side to the carbon bearing the leaving group (bromide ion).



In S_N2 mechanism



Here, in the question



So, here option (d) is correct.

04 Given below are two statements.

Statement I Ethyl pent–4–yn–oate on reaction with CH_3MgBr gives a 3° alcohol.

Statement II In this reaction, one mole of ethyl pent–4–yn–oate utilizes two moles of CH_3MgBr .

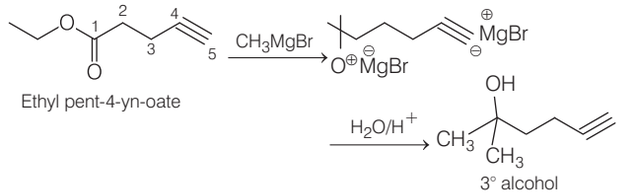
In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 27 Aug Shift-II]

(a) Both statement I and statement II are false.
(b) Statement I is false but statement II is true.
(c) Statement I is true but statement II is false.
(d) Both statement I and statement II are true.

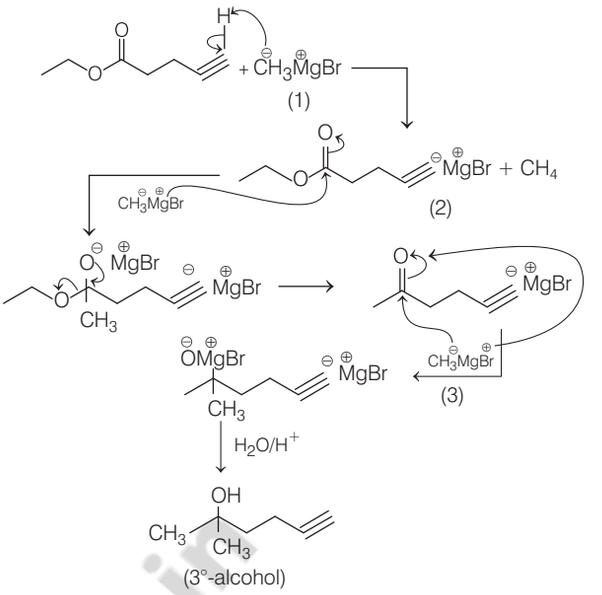
Ans. ***(c)***

Ethyl pent-4-yn-oate on reaction with CH_3MgBr gives 3° alcohol.



∴ Statement I is true.

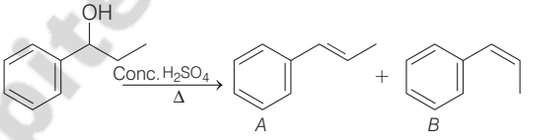
Mechanism



3 molecules of CH_3MgBr is used for this conversion.

∴ Statement II is false.

05

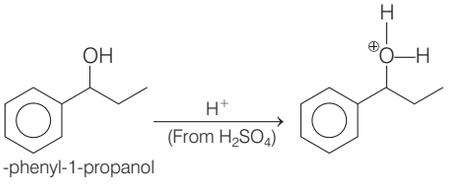


Consider the above reaction, and choose the correct statement. **[2021, 27 July Shift-II]**

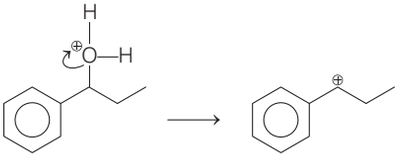
(a) The reaction is not possible in acidic medium.
(b) Both compounds *A* and *B* are formed equally.
(c) Compound *A* will be the major product.
(d) Compound *B* will be the major product.

Ans. ***(c)***

(i) Complete mechanism of given reaction is as follows:
Hydrolysis process Acid catalysed hydration of alcohol group.



(ii) Removal of water molecule/formation of carbocation.



(iii) Removal of corresponding hydrogen ion by HSO_4^- and formation of *cis* and *trans* 1-phenyl-1-propene.

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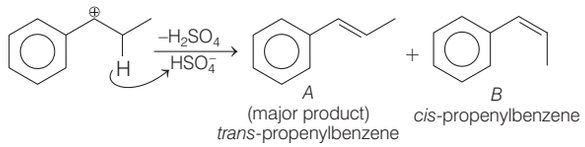
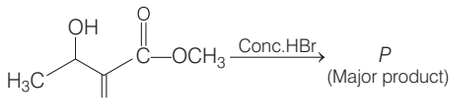
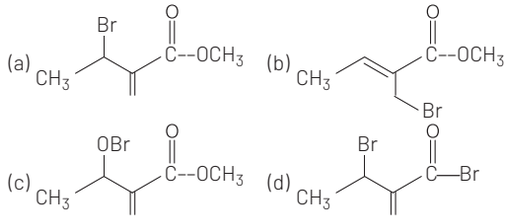


trans alkenes are more stable than *cis* alkene, so product *A* is major product formed in the reaction.

06



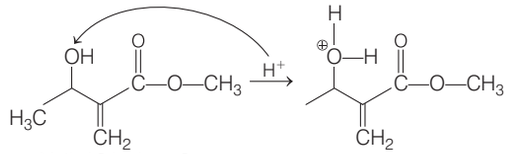
Consider the above reaction, the major product *P* formed is **[2021, 27 July Shift-II]**



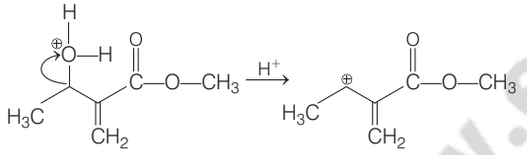
Ans. ***(b)***

Complete reaction with mechanism is as follows

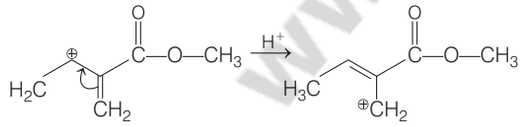
(i) Hydrolysis process Attack of H^+ on OH^- ion.



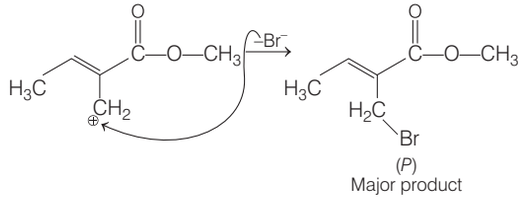
(ii) Removal of water molecule/formation of carbocation.



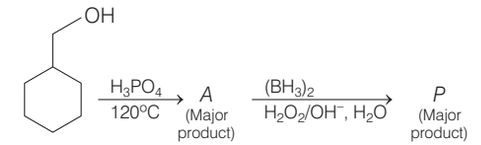
(iii) Resonance Movement of double bond/shifting of carbocation.



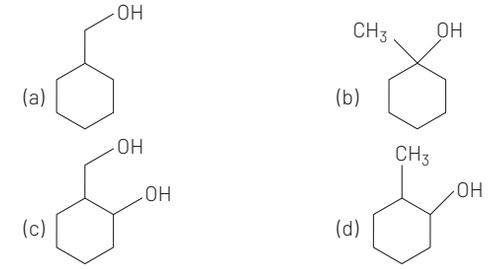
(iv) Addition of bromide ion.



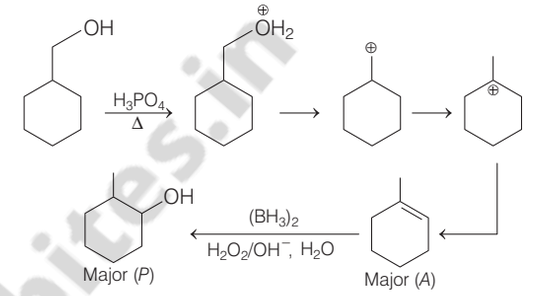
07



Consider the above reaction and identify the product (*P*). **[2021, 27 July Shift-I]**



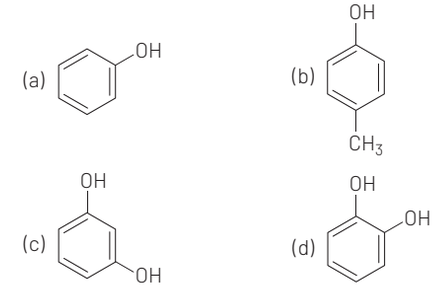
Ans. ***(d)***



Formation of compound (*A*) takes place by dehydration of alcohol by *E'* reaction.

Conversion of compound *A* to compound *P* in undergoes through hydroboration-oxidation reaction that converts an alcohol into an alcohol. In this process, H-attached at more hindered site while OH attached at less hindered site.

08 Which one of the following phenols does not give colour when condensed with phthalic anhydride in presence of conc. H_2SO_4 ? **[2021, 26 Aug Shift-II]**



Ans. ***(b)***

In the electrophilic substitution reaction, phenol gives *ortho* and *para* substituted product in which *para* is the major product. The electrophilic substitution reaction of phthalic anhydride with phenol is taking place at *para* position of the phenol. All the given molecules have free *para* position except in *p*-cresol. Hence, it does not give colour of phthalic anhydride.

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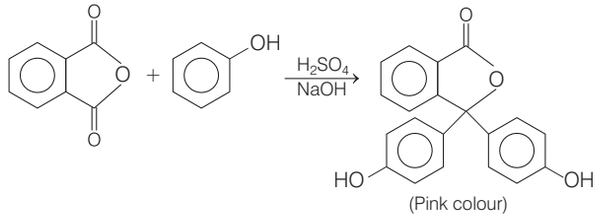
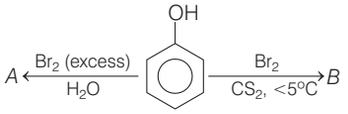
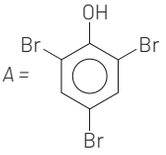
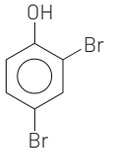
The reaction is as follows :

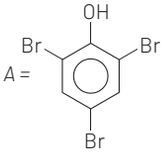
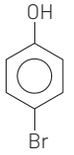


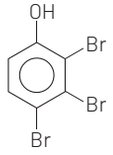
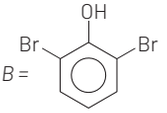
(Pink colour)

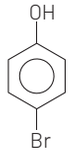
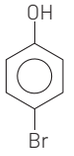
09 The correct options for the products *A* and *B* of the following reactions are **[2021, 26 Aug Shift-I]**



(a) *A* =  , *B* = 

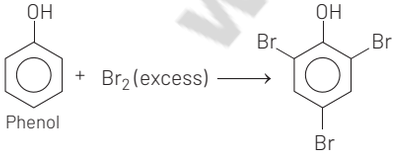
(b) *A* =  , *B* = 

(c) *A* =  , *B* = 

(d) *A* =  , *B* = 

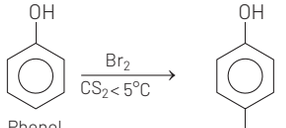
Ans. ***(b)***

Bromination of phenol with excess of bromine and water will result in multiple substitution around ring as water ionises phenol to phenoxide ion, which activities the ring for trisubstitution, while less polar solvent, i.e. CS_2 will give mono-substituted compound.



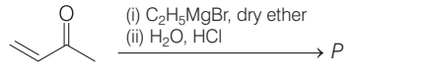
Phenol

(*A*)
2,4,5 tribromophenol



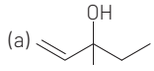
Phenol

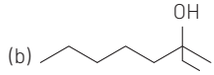
(*B*)
mono-substituted product

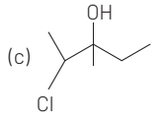
10 

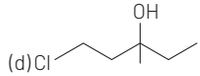
(Major product)

Consider the above reaction, the major product *P* is **[2021, 25 July Shift-I]**

(a) 

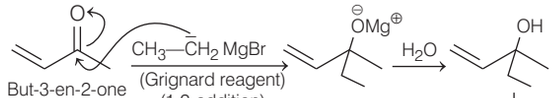
(b) 

(c) 

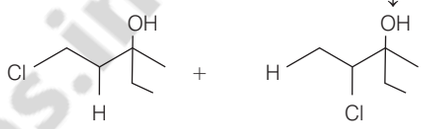
(d) 

Ans. ***(c)***

In the given reaction, Grignard reagent is used for 1, 2-addition in the carbonyl carbon and form alcohol as a major product.



But-3-en-2-one (Grignard reagent) (1,2-addition)

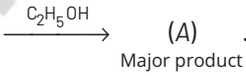


(Minor product)
1-chloro-3-methyl pentan-3-ol

(*P*)
(Major product)
1-chloro-3-methyl pentan-3-ol

Addition of HCl at the alkene gives 2-chloro-3-methylpentan-3-ol as major product.

11 In the given reaction, 3-bromo-2, 2-dimethyl butane



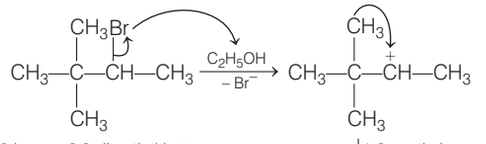
Major product .

Product *A* is **[2021, 20 July Shift-I]**

(a) 2-ethoxy-3, 3-dimethyl butane
(b) 1-ethoxy-3, 3-dimethyl butane
(c) 2-ethoxy-2, 3-dimethyl butane
(d) 2-hydroxy-3, 3-dimethyl butane

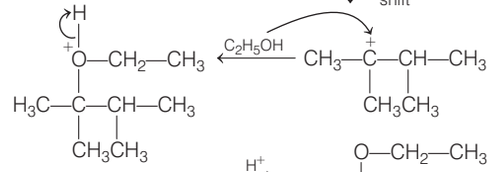
Ans. ***(c)***

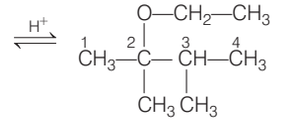
The given reaction proceeds via S_N2 reaction mechanism as follows



3-bromo-2,2-dimethyl butane

1,2, methyl shift





(*A*) (Major product)
2-ethoxy-2,3–dimethyl butane

∴ Therefore, product *A* is 2-ethoxy-2, 3-dimethyl butane.

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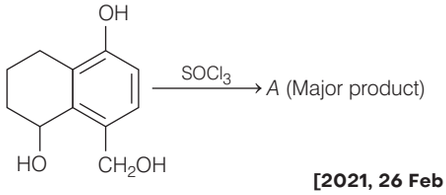
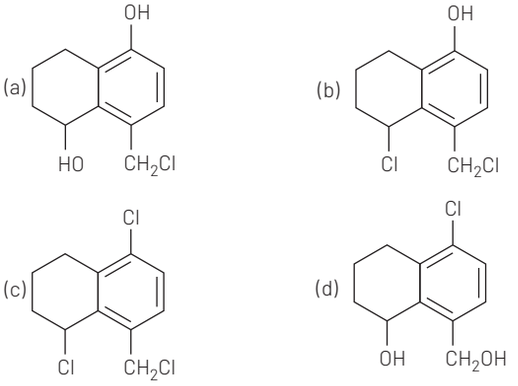
12 Identify *A* in the given reaction.



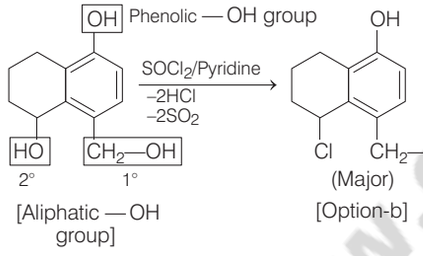
[2021, 26 Feb Shift-II]



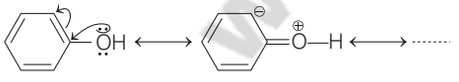
Ans. ***(b)***

The given reaction is an application of Darzen's reaction in which an aliphatic alcohol (preferably 1° or 2°) gets converted into the respective alkyl chloride (in pure form) through S_N2 pathway when it uses

pyridine or as organic base.

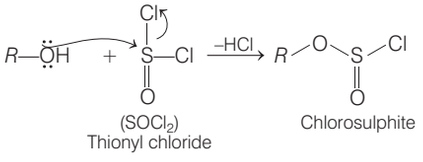


Note Phenolic — OH group does not respond to this reaction as + *R*-effect of phenolic —OH group gives double bond character to the C—O bond.

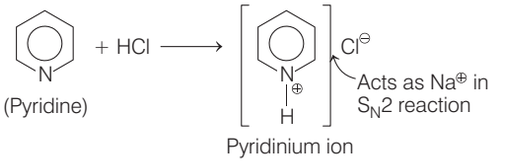


Machanism

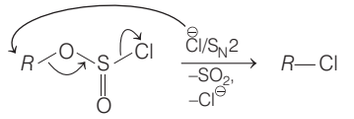
(i) Alcohol react with thionyl chloride to give chlorosulphite and HCl.



(ii) Pyridine reacts with HCl to give pyridinium chloride.



(iii) Chlorosulphite reacts with chloride ion *via*. bimolecular nucleophilic substitution reaction to give alkyl chloride.



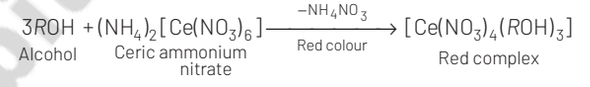
13 Ceric ammonium nitrate and $CHCl_3$ /alc. KOH are used for the identification of functional groups present in ..... and ..... respectively. **[2021, 26 Feb Shift-II]**

(a) alcohol, phenol (b) amine, alcohol
(c) alcohol, amine (d) amine, phenol

Ans. ***(c)***

Ceric ammonium nitrate and $CHCl_3$ / alc. KOH are used for the identification of functional groups present in alcohol and amine respectively.

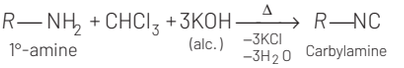
Ceric ammonium nitrate (CAN) test When an alcohol reacts with few drops of CAN, a red complex ammonium nitrate is developed which confirms presence of alcoholic —OH group.



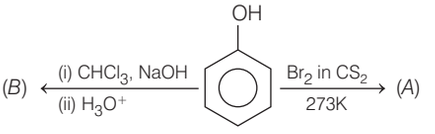
Test with $CHCl_3$ and alcoholic KOH

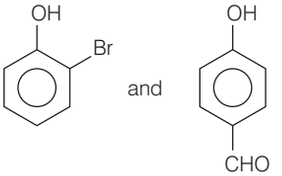
[Carbylamine test or Saytzeff's isocyanide test]

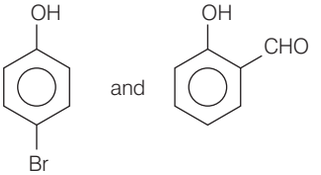
When a primary amine (aliphatic or aromatic) is heated with alcoholic KOH and chloroform ($CHCl_3$), the isocyanide (carbylamine) is formed as indicated by a foul order.



14 Identify the major products *A* and *B* respectively in the following reactions of phenol. **[2021, 26 Feb Shift-I]**



(a) 

(b) 

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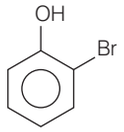
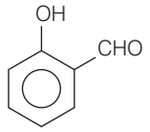
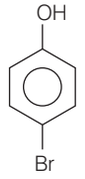
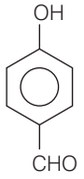
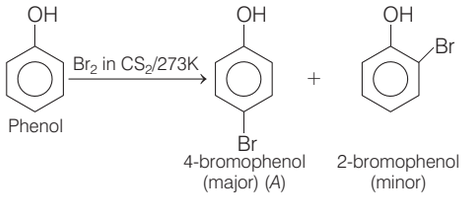
(c)  and 

(d)  and 

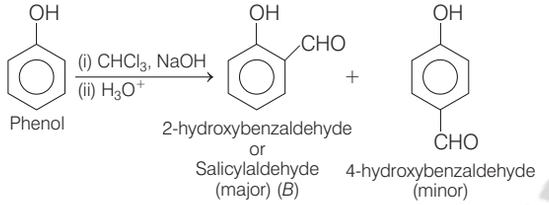
Ans. ***(b)***

Phenol on reaction with Br_2 in CS_2 / 273 K undergoes an electrophilic substitution reaction by Br^+ (electrophile) in aprotic solvent CS_2 to give 4-bromophenol as the major product.



Phenol on reaction with $CHCl_3$, NaOH followed by hydrolysis gives salicylaldehyde as a major product.

It is Reimer-Tiemann reaction. It is also an electrophilic substitution reaction of phenol by dichlorocarbene CCl_2 (electrophilic).



15 Given below are two statements:

Statement I *o*-nitrophenol is steam volatile due to intramolecular hydrogen bonding.

Statement II *o*-nitrophenol has high melting due to hydrogen bonding.

In the light of the above statements, choose the most appropriate answer from the options given below. **[2021, 26 Feb Shift-I]**

(a) Statement I is false but statement II is true

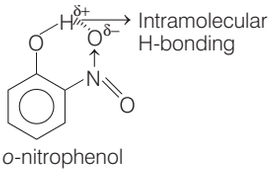
(b) Both statement I and statement II are true

(c) Both statement I and statement II are false

(d) Statement I is true but statement II is false

Ans. ***(d)***

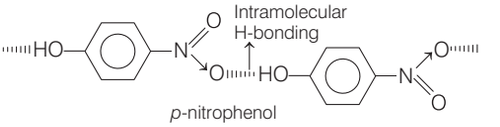
Statement I is true. Because of closer proximity (1, 2-positions) of —OH and —NO_2 groups, *o*-nitrophenol shows intramolecular hydrogen bonding.



o-nitrophenol

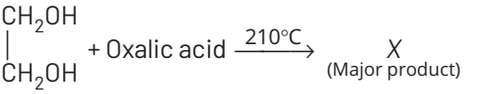
So, *o*-nitrophenol exists in monomeric state and becomes steam volatile. Statement II is false, because, due to the presence of intramolecular hydrogen bonding, boiling point and melting point of *o*-nitrophenol will be lower.

Note *p*-nitrophenol is the positional isomer of *o*-nitrophenol. *p*-nitrophenol shows intermolecular hydrogen bonding and so, it has higher boiling point, melting point and water solubility.

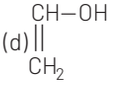


p-nitrophenol

16 What is '*X*' in the given reaction?

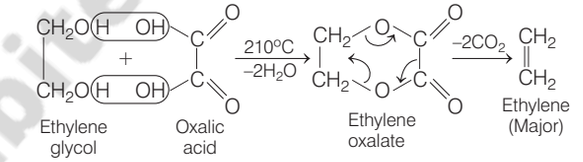


[2021, 25 Feb Shift-II]

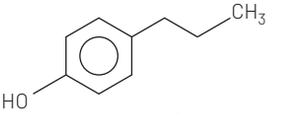
(a) (b) (c) (d) 

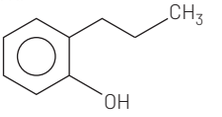
Ans. ***(c)***

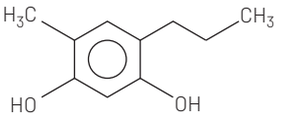
When ethylene glycol is heated with oxalic acid at 210ºC, first we get an unstable cyclic-diester (ethylene oxalate) which readily decarboxylate to give ethylene as the major product.

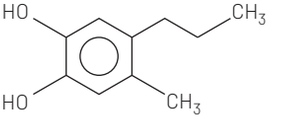


17 Which of the following compound gives pink colour on reaction with phthalic anhydride in conc. H_2SO_4 followed by treatment with NaOH? **[2021, 24 Feb Shift-I]**

(a) 

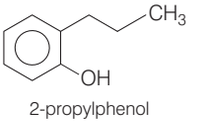
(b) 

(c) 

(d) 

Ans. ***(b)***

Correct answer is



2-propylphenol

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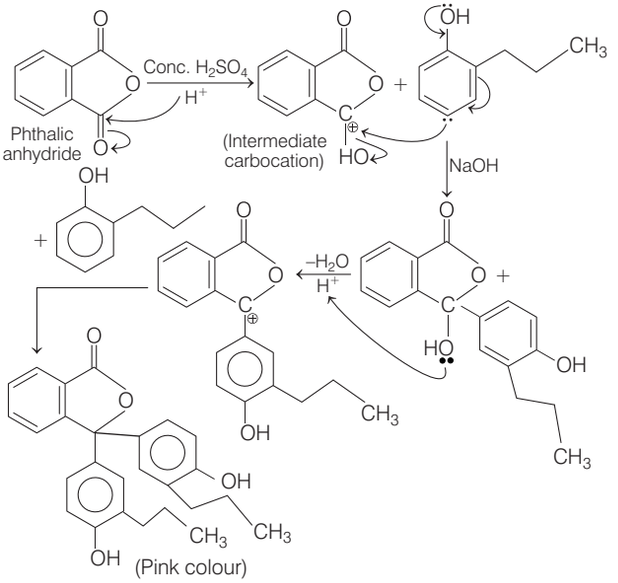
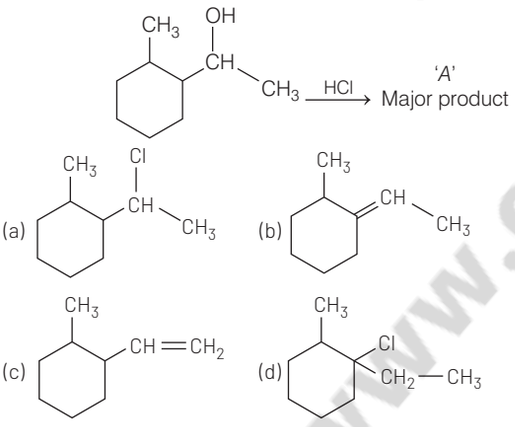
Firstly phthalic anhydride in presence of conc. H_2SO_4 undergoes protonation to give an intermediate carbocation. This carbocation reacts with 2-propylphenol in presence of NaOH to give pink colour compound.

Mechanism



2-propylphenol gives pink colour on reaction with phthalic anhydride in conc. followed by treatment with NaOH.

18 What is the final product (major) '*A*' in the given reaction? **[2021, 24 Feb Shift-I]**

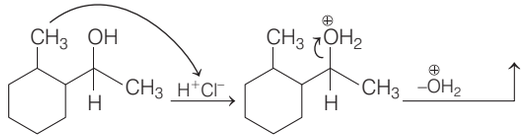


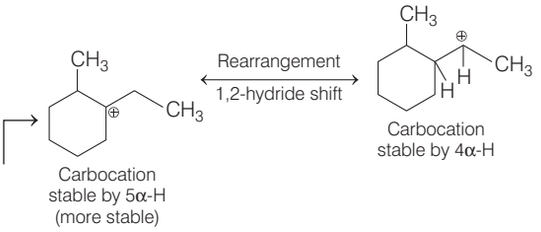
Ans. ***(d)***

Steps involved in this reaction are as follows

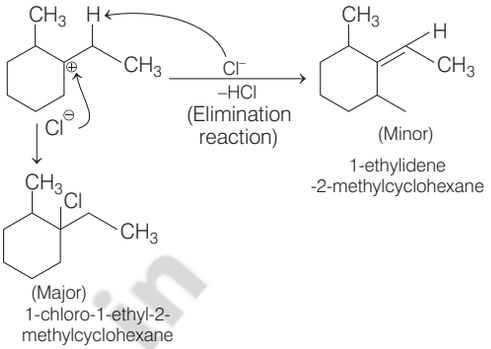
Step 1 $HCl \longrightarrow H^+ + Cl^-$

H^+ attacks on –OH (lone pair) and formed $\overset{\oplus}{O}H_2$ ion. Here, $\overset{\oplus}{O}H_2$ is the good leaving group.





Step 2 Elimination reaction always give minor product than substitution reaction.



19 Two compounds *A* and *B* with same molecular formula (C_3H_6O) undergo Grignard's reaction with methylmagnesium bromide to give products *C* and *D*. Products *C* and *D* show following chemical tests.

Test	*C*	*D*
Ceric ammonium nitrate test	Positive	Positive
Lucas test	Turbidity obtained after five minutes	Turbidity obtained immediately
Iodoform test	Positive	Negative

C and *D* respectively are **[2020, 2 Sep Shift-II]**

(a) $C = H_3C—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$; $D = H_3C—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$

(b) $C = H_3C—CH_2—CH_2—CH_2—OH$;

$D = H_3C—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

(c) $C = H_3C—CH_2—CH_2—CH_2—OH$; $D = H_3C—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$

(d) $C = H_3C—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$; $D = H_3CCH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

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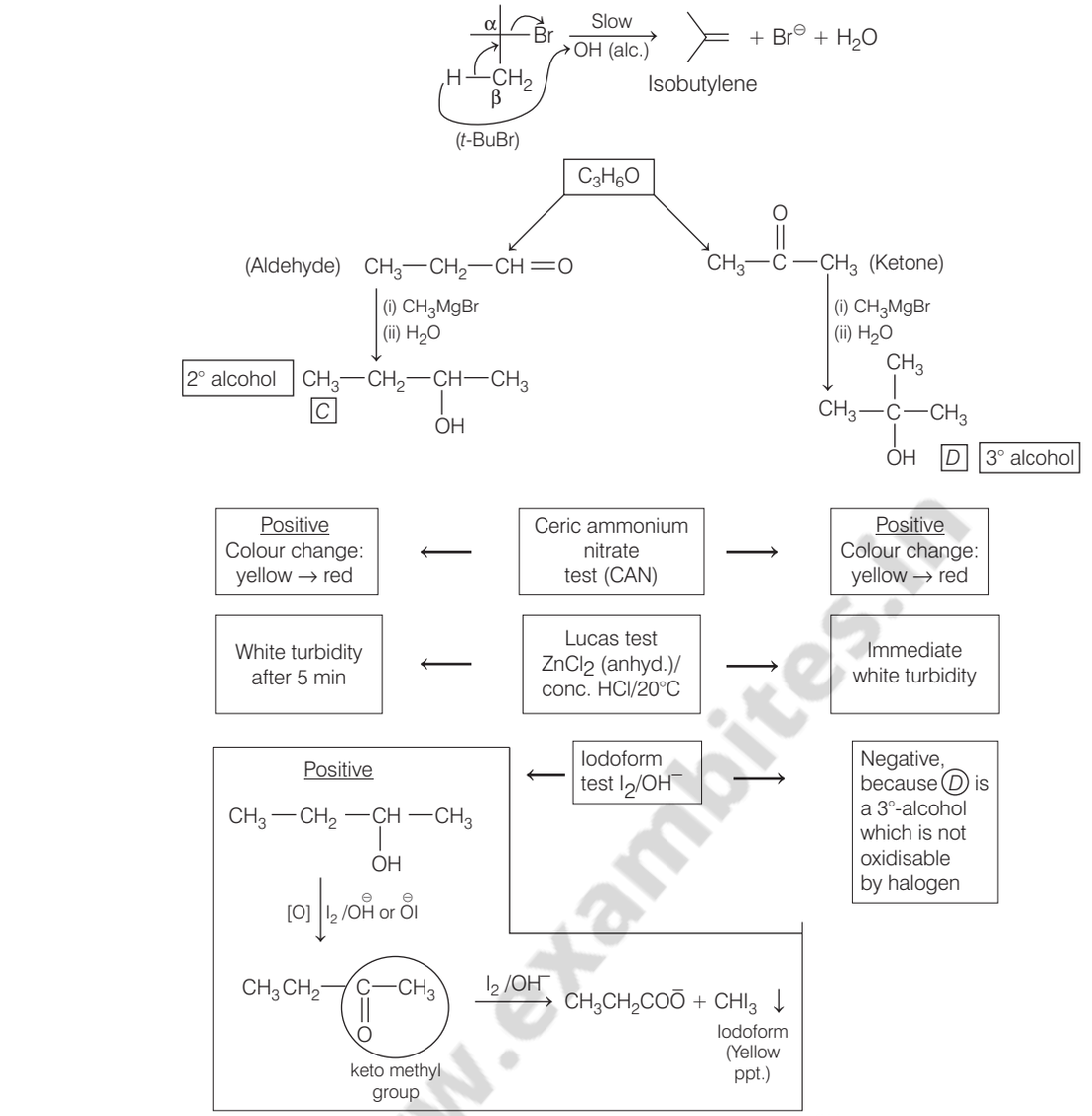
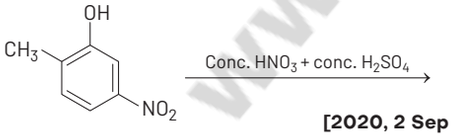
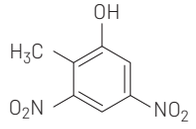
Ans. ***(a)***

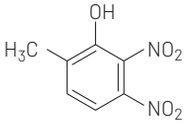


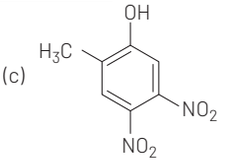
20 The major product of the following reaction is

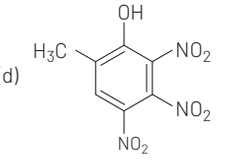


[2020, 2 Sep Shift-II]

(a) 

(b) 

(c) 

(d) 

Ans. ***(c)***

The substrate undergoes nitration reaction ($ArSE_2$). The electrophile (NO_2^+) will prefer to attack benzene nucleus which is rich with electron density (by $+R$ or $+I$-effect of substituent, where $+R > +I$) as wall as sterically less crowded.

Out of three substituents, the —OH group will dominate the rate of initiation reaction, because —OH has strong ring activating property by its $+R$ or $+M$ effect.

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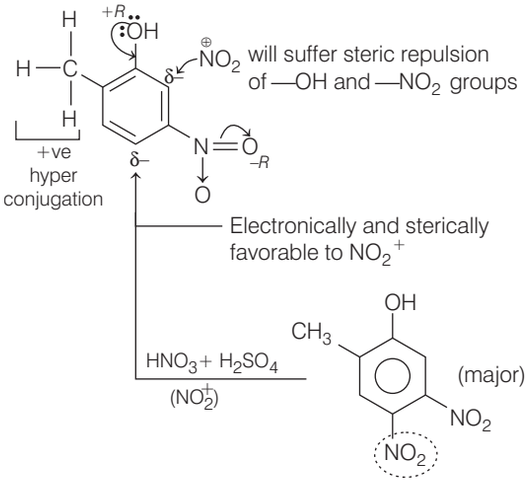
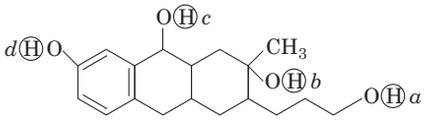
The ring activating order is

$$-OH \underset{(+R\text{ effect})}{>} -CH_3 \underset{\text{conjugation})}{>} -NO_2 \underset{(-R\text{ effect})}{}$$



21 Consider the following reaction :



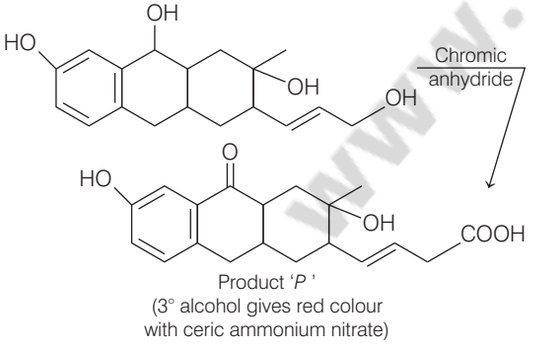
$\xrightarrow[\text{anhydride}]{\text{Chromic}}$ *'P'* The product *'P'* gives positive ceric ammonium nitrate test. This is because of the presence of which of these —OH group(s)?

[2020, 3 Sep Shift-II]

(a) (b) and (d) (b) (d) only
(c) (b) only (d) (c) and (d)

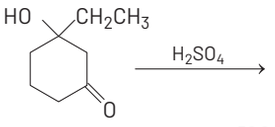
Ans. ***(c)***

Only 3° alcohol give positive ceric ammonium nitrate test.

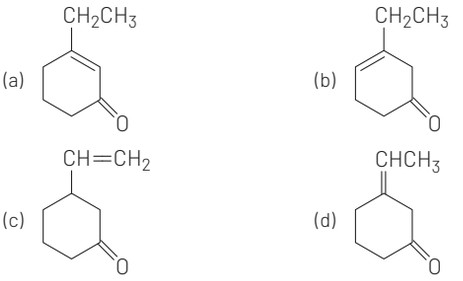


Product *'P'*
(3° alcohol gives red colour with ceric ammonium nitrate)

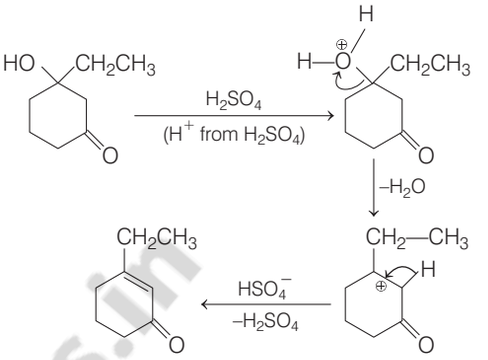
22 The major product of the following reaction is



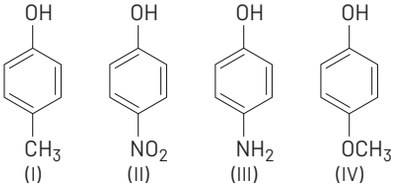
[2020, 5 Sep Shift-II]



Ans. ***(a)***



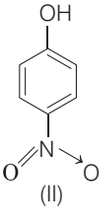
23 The increasing order of boiling points of the following compounds is



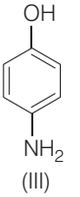
[2020, 5 Sep Shift-II]

(a) I < III < IV < II (b) I < IV < III < II
(c) IV < I < II < III (d) III < I < II < IV

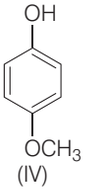
Ans. ***(b)***



shows strongest hydrogen bonding from —OH group.



shows stronger hydrogen bonding from both side of —OH group as well as —NH_2 group.



shows stronger hydrogen bonding from one side —OH group and another side of —OCH_3 group shows only dipole-dipole interaction.

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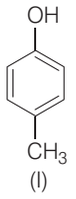
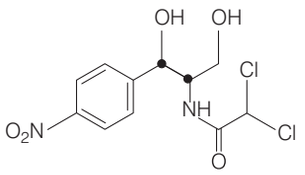

(I)

Boiling point μ dipole moment (μ). shows hydrogen bonding from —OH group only.

24 The number of chiral carbons in chloramphenicol is ..... .
[2020, 7 Jan Shift-I]

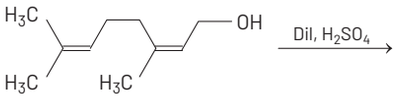
Ans. ***(2.00)***

Structure of chloramphenicol is

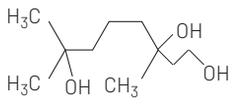


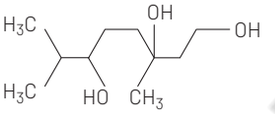
The two carbon atoms shown by black circles are chiral.

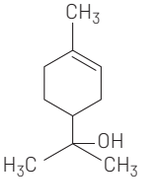
25 The major product of the following reaction is :

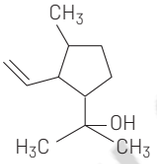


[2020, 8 Jan Shift-I]

(a) 

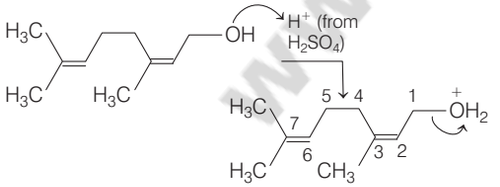
(b) 

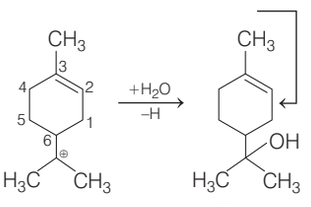
(c) 

(d) 

Ans. ***(c)***

The reaction proceeds as follows:





(Torpineol)

26 Arrange the following compounds in increasing order of C—OH bond length : methanol, phenol, *p*-ethoxyphenol
[2020, 8 Jan Shift-I]

(a) phenol < methanol < *p*-ethoxyphenol
(b) phenol < *p*-ethoxyphenol < methanol
(c) methanol < *p*-ethoxyphenol < phenol
(d) methanol < phenol < *p*-ethoxyphenol

Ans. ***(b)***

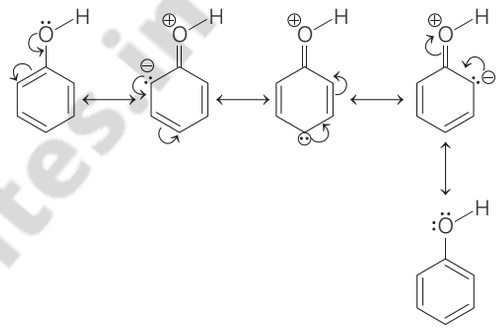
The increasing order of C—OH bond length in the given compounds is : phenol < *p*-ethoxy phenol < methanol. It is explained as follows:

Methanol has no resonance and no partial double bond character in C—OH bond.

∴ It has maximum C—OH bond length.

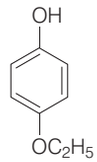
In both phenol and *p*-ethoxyphenol, resonance is involved.

∴ C—OH bond has partial double bond character and hence C—OH bond length is less than methanol.



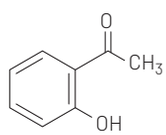
(*p*-ethoxyphenol also exhibits similar resonating structures).

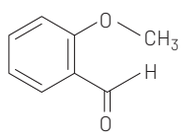
But in *p*-ethoxyphenol, there is + *R*-effect of 'OC_2H_5' group also.



So the 'C—OH' bond has less double bond character and slightly more bond length than C—OH bond length in phenol.

27 An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution. It however, reacts with Grignard reagent and gives positive iodoform test. The compound is **[2019, 8 April Shift-I]**

(a) 

(b) 

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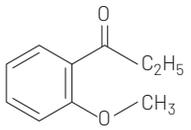
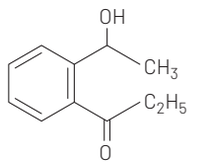
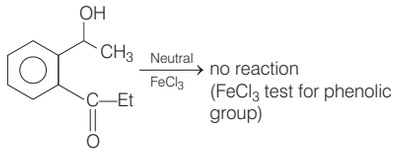
(c) 

(d) 

Ans. ***(d)***

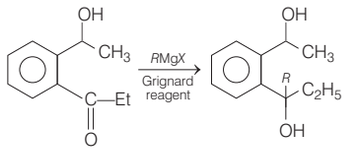
According to the given conditions, compound (d) neither reacts with neutral ferric chloride solution nor with Fehling solution. It however reacts with Grignard reagent and gives positive iodoform test.

- As the compound does not contain any phenolic —OH group. Hence, it gives negative neutral $FeCl_3$ test.

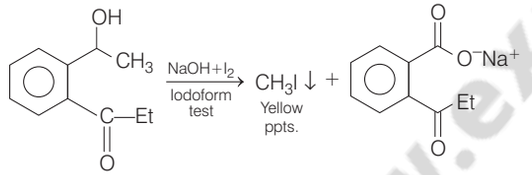


- Compound gives reaction with

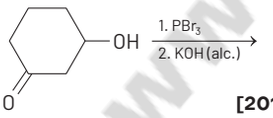
*R*Mg*X* as it contains



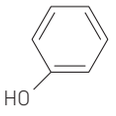
Compound with $CH_3\underset{\underset{OH}{|}}{CH}-$ group undergoes iodoform test in presence of NaOH and I_2.

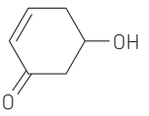


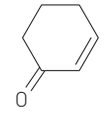
28 The major product of the following reaction is

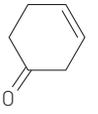


[2019, 9 April Shift-I]

(a) 

(b) 

(c) 

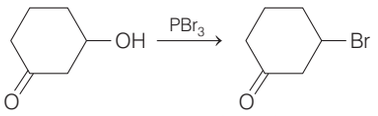
(d) 

Ans. ***(c)***

Key Idea PBr_3 reagent is used for the substitution of —Br group while alc. KOH reagent is used to carry out elimination reaction.

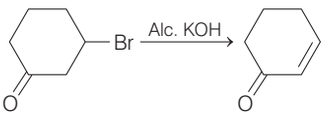
The given reaction proceed in following manner:

Step I In presence of PBr_3, alcohols undergo substitution reactions to give halides. Reagent PBr_3 is usually generated *insitu* by the reaction of red phosphorus with bromine.



3-bromohexanone

Step II 3-bromohexanone in presence of alc. KOH undergoes elimination reaction and gives cyclohex-2-en-1-one.



Cyclohex-2-en-1-one

29 The major product of the following reaction is

$CH_3CH=CHCO_2CH_3 \xrightarrow{LiAlH_4}$ **[2019, 9 April Shift-I]**

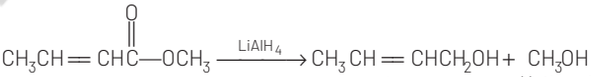
(a) $CH_3CH=CHCH_2OH$ (b) $CH_3CH_2CH_2CH_2OH$

(c) $CH_3CH_2CH_2CO_2CH_3$ (d) $CH_3CH_2CH_2CHO$

Ans. ***(a)***

Key Idea $LiAlH_4$ reagent is used for the reduction of $-\overset{\overset{O}{\|}}{C}OCH_3$. It does not reduce double bonds.

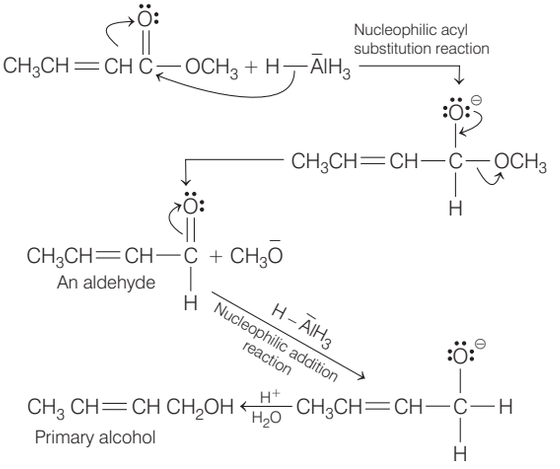
The reaction of an ester with $LiAlH_4$ produces two alcohols, one corresponding to the acyl portion of the ester and one corresponding to the alkyl portion.



Thus, the major product of the given reactant $CH_3CH=CH-\overset{\overset{O}{\|}}{C}OCH_3$ in presence of $LiAlH_4$ is $CH_3CH=CHCH_2OH$ and CH_3OH.

The reaction proceeds through following mechanism.

Mechanism



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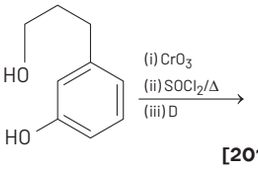
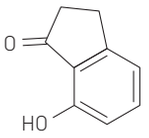
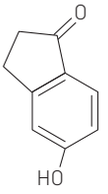
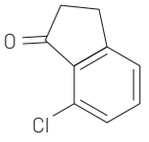
30 The major product of the following reaction is

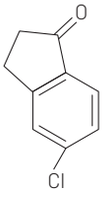


[2019, 12 April Shift-I]

(a) 

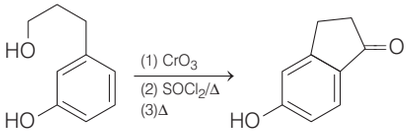
(b) 

(c) 

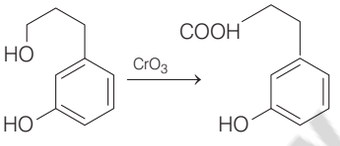
(d) 

Ans. ***(b)***

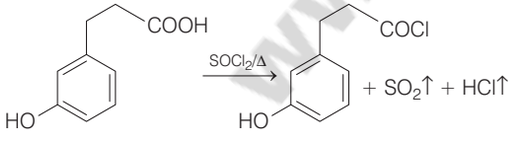
The major product formed in the reaction is as follows:



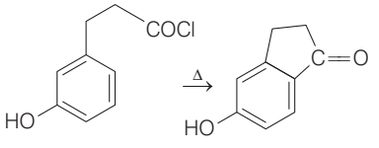
Primary alcohol readily oxidised to corresponding carboxylic acid with oxidising agent, chromium trioxide (CrO_3) in acidic medium.



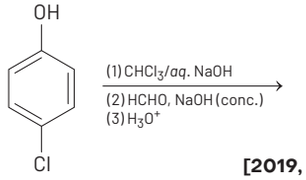
—OH group of carboxylic acid get substituted by —Cl in presence of $SOCl_2$ (Thionyl chloride).



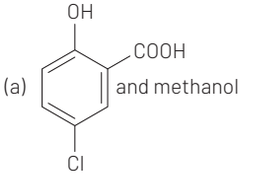
Further, heating of product leads to intramolecular cyclisation.

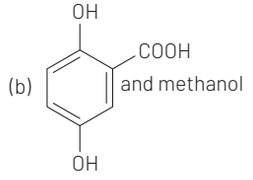


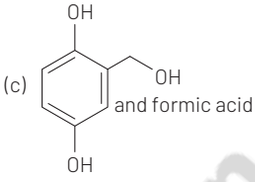
31 The major products of the following reaction are

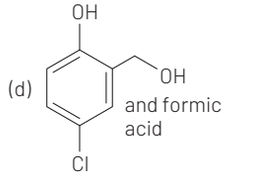


[2019, 12 April Shift-I]

(a) 

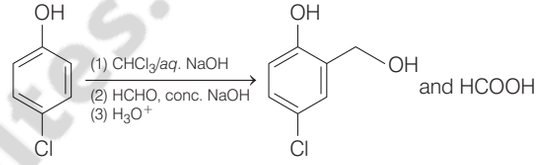
(b) 

(c) 

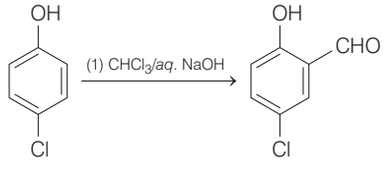
(d) 

Ans. ***(d)***

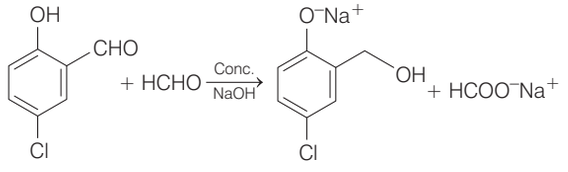
The major products of the given reaction are as follows:



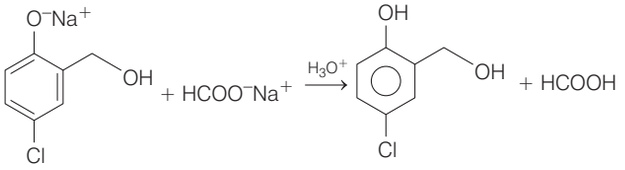
In step-I, substituted phenol undergoes Reimer- Tiemann reaction in presence of $CHCl_3$ / *aq*. NaOH



The aldehyde obtained in above equation does not possess α-hydrogen. In presence of formaldehyde and conc. NaOH it undergoes Cannizaro reaction. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.



Upon hydrolysis, following reaction takes place



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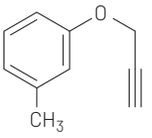
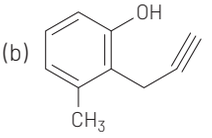
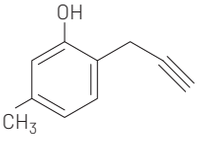
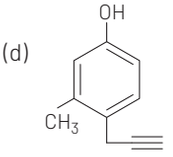
32 What will be the major product when *m*-cresol is reacted with propargyl bromide ($HC \equiv C—CH_2Br$) in presence of K_2CO_3 in acetone? **[2019, 12 April Shift-II]**

(a) 

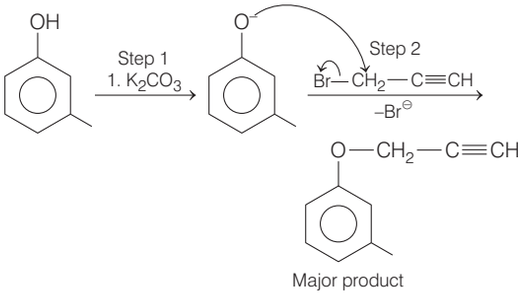
(b) 

(c) 

(d) 

Ans. ***(a)***

The major product when *m*-cresol reacts with propargyl bromide ($HC \equiv C—CH_2Br$) in presence of K_2CO_3 in acetone is given in the following reaction:

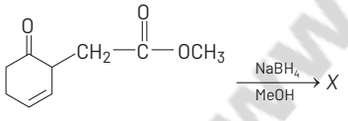


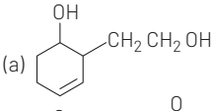
In step 1 K_2CO_3 act as a base and abstract H-atom from —OH group.

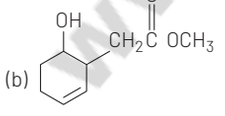
This leads to the formation of substituted phenoxide ion (highly stable).

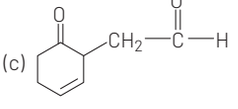
In step 2 substituted phenoxide ion on reaction with $Br—CH_2—C \equiv CH$ gives the required product.

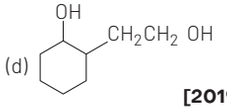
33 The major product '*X*' formed in the following reaction is



(a) 

(b) 

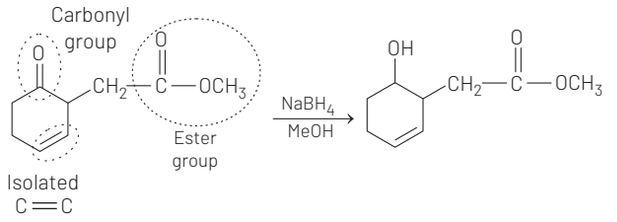
(c) 

(d) 

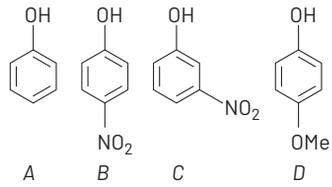
[2019, 10 Jan Shift-I]

Ans. ***(b)***

$NaBH_4$ is a selective reducing agent. It reduces carbonyl $\left(\rangle C = O\right)$ group into an alcohol but cannot reduce an isolated $C = C$ and an ester group too.



34 The increasing order of the pK_a values of the following compounds is **[2019, 10 Jan Shift-I]**



(a) *D* < *A* < *C* < *B*
(b) *B* < *C* < *A* < *D*
(c) *C* < *B* < *A* < *D*
(d) *B* < *C* < *D* < *A*

Ans. ***(b)***

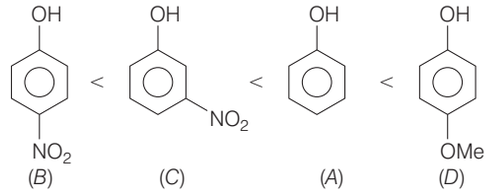
Acidic strength is inversely proportional to pK_a value. The acidity of phenols is due to greater resonance stabilisation of phenoxide ion relative to phenol.

Therefore, any substituent which stabilises the phenoxide ion more by dispersal of negative charge will tend to increase the acidity of phenol.

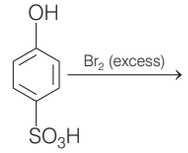
Electron withdrawing groups (—NO_2) increases the acidic strength of phenol whereas electron donating group (—OCH_3) decreases the acidic strength of phenol. In case of —NO_2 group attached to phenol, the dispersal of negative charge is more pronounced at *o*- and *p*-position than at *m*-position.

Thus, order of acidic strength of nitrophenol is:

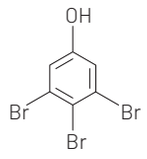
p-nitrophenol > *o*-nitrophenol and the correct order of the pK_a values of give option is

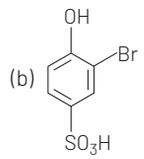


35 The major product of the following reaction is



[2019, 11 Jan Shift-I]

(a) 

(b) 

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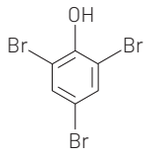
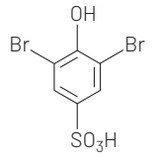
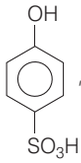
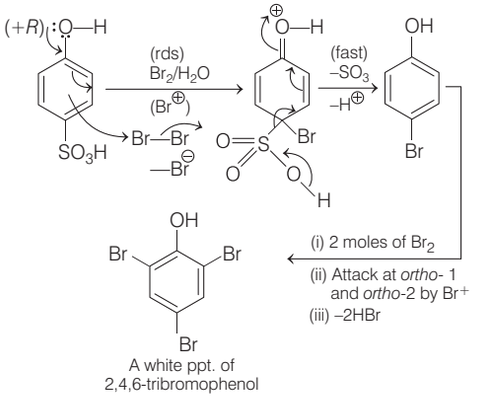
(c) 

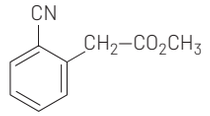
(d) 

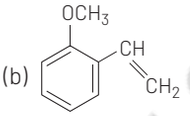
Ans. ***(c)***

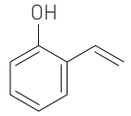
In  , *ipso*-substitution takes place with the carbon bearing $-SO_3H$ group. After the attack of the electrophilic Br^+ in the rate determining step (rds) of the $Ar S_E2$ pathway desulphonation ($-SO_3$) takes place with a faster rate.

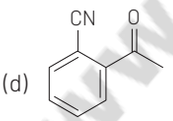


36 Which of the following compounds reacts with ethyl magnesium bromide and also decolourises bromine water solution **[2019, 11 Jan Shift-II]**

(a) 

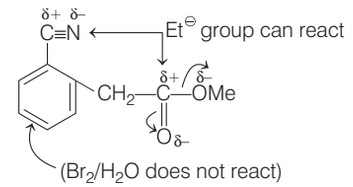
(b) 

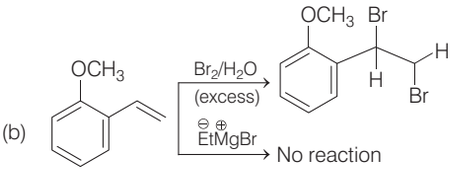
(c) 

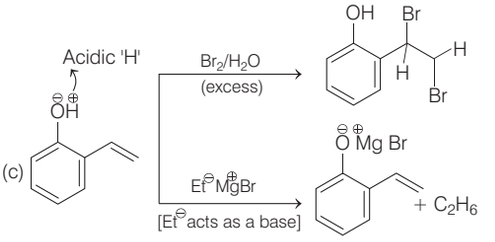
(d) 

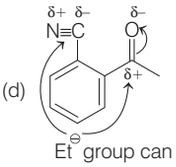
Ans. ***(c)***

Ethyl magnesium bromide is a Grignard reagent (GR), it constitutes $C_2H_5^-$ [$C_2H_5^-\overset{\oplus}{M}gBr$ in ether/aprotic medium] which can act as nucleophile as well as strong base. Bromine water (Br_2/H_2O, red) gets decolourised with phenol derivatives (option, c), anisole derivatives (option, b) etc., as $>C=C<$ is present outside the ring (aliphatic, not aromatic).

(a) 

(b) 

(c) 

(d) 

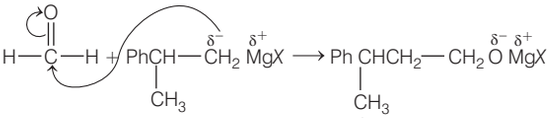
37 $CH_3CH_2-\underset{\underset{Ph}{|}}{\overset{OH}{\overset{|}{C}}}-CH_3$ cannot be prepared by **[2019, 12 Jan Shift-I]**

(a) $CH_3CH_2COCH_3 + PhMgX$ (b) $PhCOCH_3 + CH_3CH_2MgX$

(c) $PhCOCH_2CH_3 + CH_3MgX$ (d) $HCHO + PhCH(CH_3)CH_2MgX$

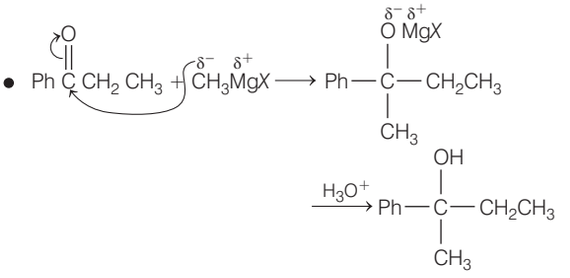
Ans. ***(d)***

$CH_3CH_2-\underset{\underset{Ph}{|}}{\overset{OH}{\overset{|}{C}}}-CH_3$ cannot be prepared by HCHO and $PhCH(CH_3)CH_2MgX$. This can be easily illustrated by following reaction.



The obtained product is not the required substance. While option (a), (b) and (c) can readily prepare the required substance.

The reactions are as follows :



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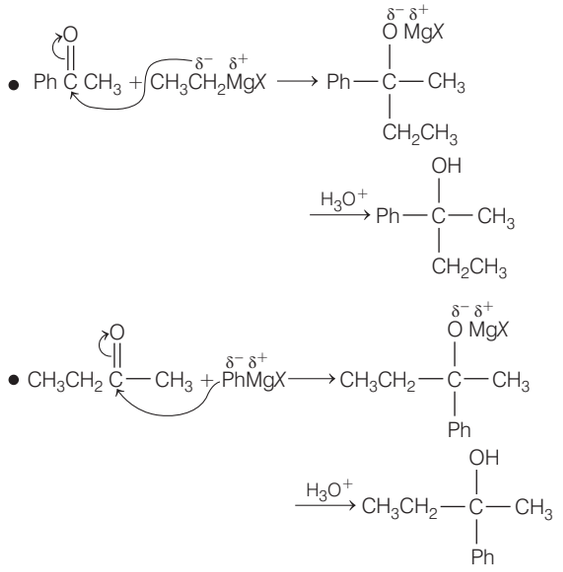
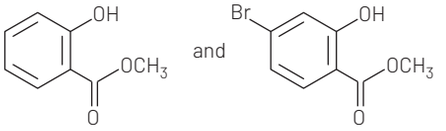
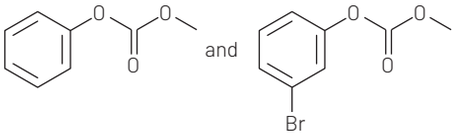
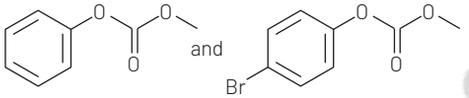
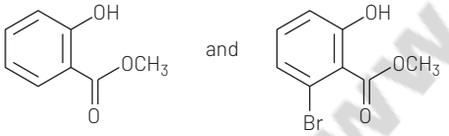


38 Phenol reacts with methyl chloroformate in the presence of NaOH to form product *A*. *A* reacts with Br_2 to form product *B*. *A* and *B* are respectively **[JEE Main 2018]**

(a) 

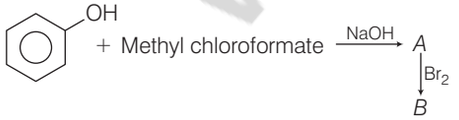
(b) 

(c) 

(d) 

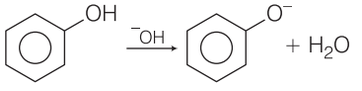
Ans. ***(c)***

Given

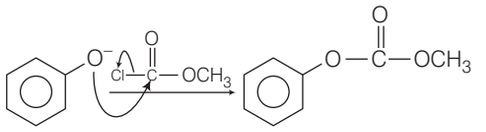


In the above road map, first reaction appears as acid base reaction followed by S_NAE(Nucleophilic substitution through Addition and Elimination). Both the steps are shown below

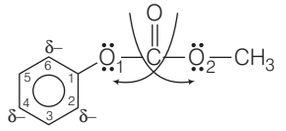
(i) **Acid base reaction**



(ii) S_NAE

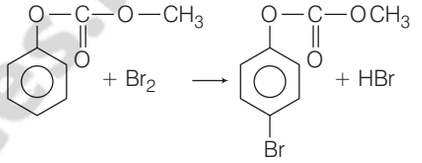


In the product of S_NAE the attached group is *ortho* and *para*-directing due to following cross conjugation

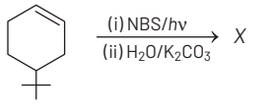


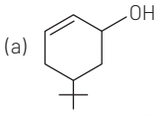
Cross conjugation due to which lone pair of oxygen 1 will be easily available to ring resulting to higher electron density at 2, 4, 6 position with respect to group. However from the stability point of view *ortho* positions are not preferred by substituents as group —O—C—O—CH_3 is bulky.

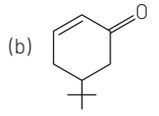
Hence, on further bromination of S_NAE product *para* bromo derivative will be the preferred product i.e.

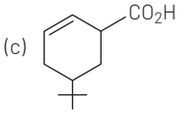


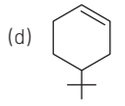
39 The product of the reaction given below is **[JEE Main 2016]**



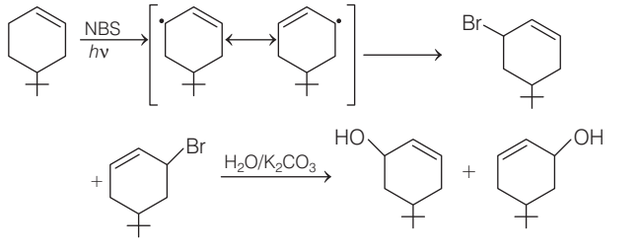
(a) 

(b) 

(c) 

(d) 

Ans. ***(a)***



40 The most suitable reagent for the conversion of $R—CH_2—OH \rightarrow R—CHO$ is **[JEE Main 2014]**

(a) $KMnO_4$ (b) $K_2Cr_2O_7$

(c) CrO_3

(d) PCC [Pyridinium chlorochromate]

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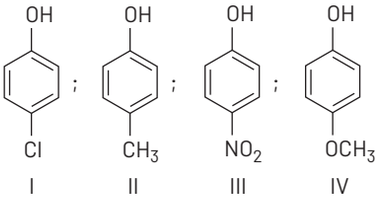
Ans. ***(d)***

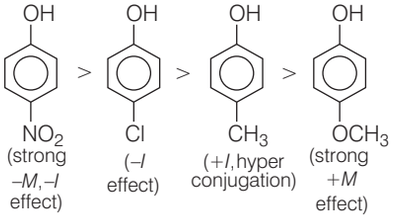
Mild oxidising agents like PCC [Pyridinium chlorochromate] are particularly used for the conversion of $R - CH_2OH \rightarrow R - CHO$.

41 Arrange the following compounds in the order of decreasing acidity **[JEE Main 2013]**



(a) II > IV > I > III (b) I > II > III > IV
(c) III > I > II > IV (d) IV > III > I > II

Ans. ***(c)***



Electron releasing group decreases while electron withdrawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.

42 An unknown alcohol is treated with the 'Lucas reagent' to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism? **[JEE Main 2013]**

(a) Secondary alcohol by S_N1
(b) Tertiary alcohol by S_N1
(c) Secondary alcohol by S_N2
(d) Tertiary alcohol by S_N2

Ans. ***(b)***

The reaction of alcohol with Lucas reagent is mostly S_N1 reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction.

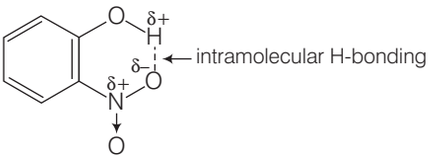
Since 3° *R*—OH forms 3° carbocation (most stable) hence it will react fastest by S_N1 reaction.

43 *Ortho*-nitrophenol is less soluble in water than *p*- and *m*-nitrophenols because

(a) *o*-nitrophenol is more volatile steam than those of *m*- and *p*-isomers.
(b) *o*-nitrophenol shows intramolecular H-bonding
(c) *o*-nitrophenol shows intermolecular H-bonding
(d) melting point of *o*-nitrophenol is lower than those of *m*- and *p*-isomers **[AIEEE 2012]**

Ans. ***(b)***

There is intramolecular H-bonding in *o*-nitrophenol and thus solubility in water is decreased.



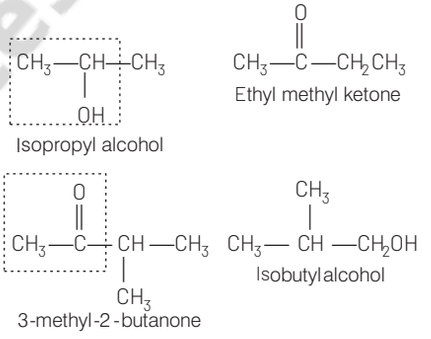
44 Iodoform can be prepared from all except

(a) ethyl methyl ketone **[AIEEE 2012]**
(b) isopropyl alcohol
(c) 3-methyl-2-butanone
(d) isobutyl alcohol

Ans. ***(d)***

Iodoform reaction is given by alcohols and ketones containing $CH_3-\underset{\underset{OH}{|}}{CH}-$ and $CH_3-\overset{\overset{O}{\|}}{C}-$ group, respectively. Thus, among the given compounds, isobutyl alcohol does not contain $CH_3-\underset{\underset{OH}{|}}{CH}-$ group.

Hence, it does not give iodoform reaction on treatment with I_2/NaOH.



Hence, compounds (*a*), (*b*) and (*c*) will give iodoform while compound (*d*) (isobutyl alcohol) does not give any iodoform reaction.

45 Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is **[AIEEE 2011]**

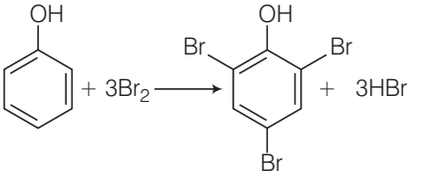
(a) 2-bromophenol (b) 3-bromophenol
(c) 4-bromophenol (d) 2, 4, 6-tribromophenol

Ans. ***(d)***

Br_2 is formed by a redox reaction.

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

—OH group is the activating group and thus activates the benzene towards electrophilic substitution reaction at *o*-and *p*-positions giving yellowish white precipitate of 2,4,6-tribromophenol.



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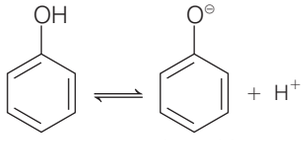
46 The correct order of acid strength of the following compounds is **[AIEEE 2011]**

I. Phenol II. *p*-cresol
III. *m*-nitrophenol IV. *p*-nitrophenol

(a) III > II > I > IV (b) IV > III > I > II (c) II > IV > I > III (d) I > II > IV > III

Ans. ***(b)***

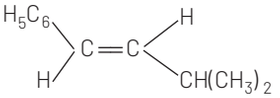
I. 

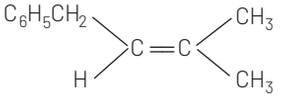
phenoxide

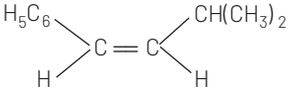
(a), (b), (d) may be formed but (c) is never formed.

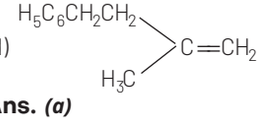
47 The main product of the following reaction is

$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{Conc. } H_2SO_4} ?$ **[AIEEE 2010]**

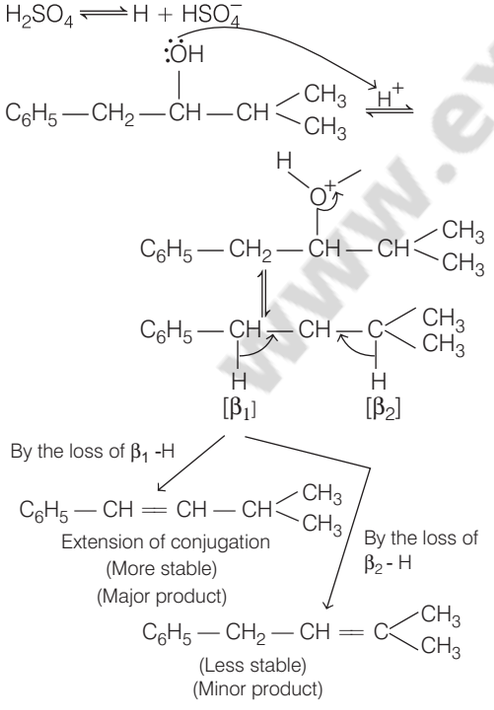
(a) 

(b) 

(c) 

(d) 

Ans. ***(a)***



48 From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$ is

(a) 2-butanol (b) 2-methylpropan-2-l
(c) 2-methylpropanol (d) 1-butanol **[AIEEE 2010]**

Ans. ***(b)***

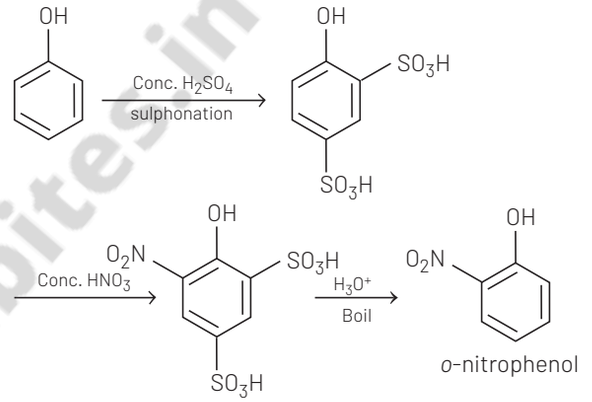
The reaction of alcohol with conc. HCl and anhydrous $ZnCl_2$ follows S_N1 pathway, so greater the stability of carbocation formed, faster is the reaction. 2-methylpropan-2-ol gives 3° carbocation.

Hence, it reacts rapidly with conc. HCl and anhydrous $ZnCl_2$ (Lucas reagent).

49 Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid gives **[AIEEE 2008]**

(a) 2, 4, 6-trinitrobenzene
(b) *o*-nitrophenol
(c) *p*-nitrophenol
(d) nitrobenzene

Ans. ***(b)***



First sulphonation is the means to block *para* and ortho position and to reduce the reactivity of phenolic ring against strong oxidising agent HNO_3. (The use of conc. HNO_3 over phenol cause the oxidation of ring mainly). — SO_3H groups are knocked out on boiling with H_2O.

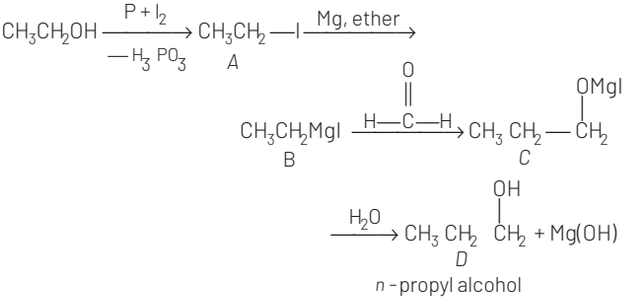
50 In the following sequence of reactions,

$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$

the compound '*D*' is **[AIEEE 2007]**

(a) butanal (b) *n*-butyl alcohol
(c) *n*-propyl alcohol (d) propanal

Ans. ***(c)***



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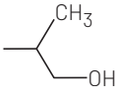
51 Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is **[AIEEE 2006]**

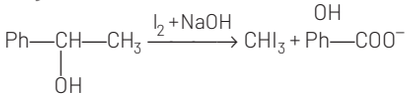
(a) $CH_3CH_2CH(OH)CH_2CH_3$ (b) $C_6H_5CH_2CH_2OH$

(c)  (d) $PhCHOHCH_3$

Ans. ***(d)***

For positive iodoform test, alcohol molecule must have $CH_3—\underset{\underset{OH}{|}}{CH}—$ group.

Thus, iodoform test is given by only (d) $Ph—\underset{\underset{OH}{|}}{CH}—CH_3$ while others will not give this test.

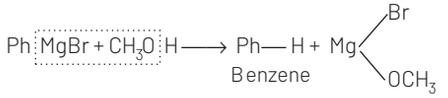


52 Phenyl magnesium bromide reacts with methanol to give **[AIEEE 2006]**

(a) a mixture of anisol and Mg(OH)Br
(b) a mixture of benzene and Mg(OMe)Br
(c) a mixture of toluene and Mg(OH)Br
(d) a mixture of phenol and Mg(Me)Br

Ans. ***(b)***

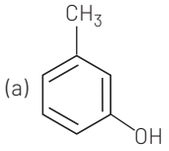
PhMgBr can be protonated by any of the protic solvent *e.g.*, CH_3OH.

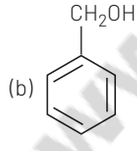


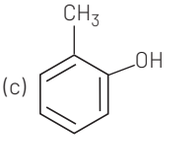
Benzene

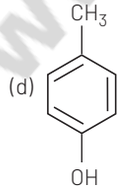
Methoxy magnesium bromide

53 The structure of the compound that gives a tribromo derivative on treatment with bromine water is **[AIEEE 2006]**

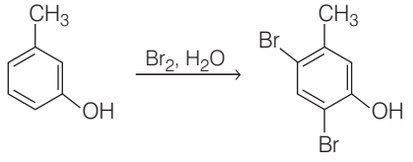
(a) 

(b) 

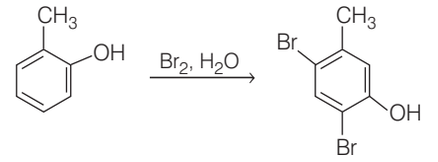
(c) 

(d) 

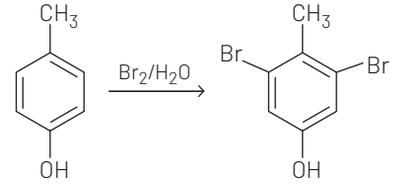
Ans. ***(a)***

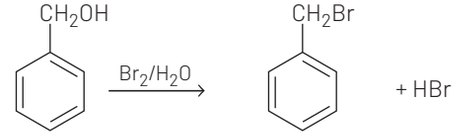


Tribromo derivative

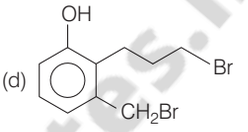
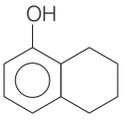


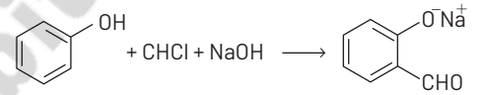
Dibromo derivative





m-cresol due to phenoxide ion in H_2O solvent, gives tribromoderivative at all *ortho and para* positions.

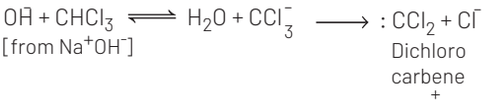
(d)  and 

54 

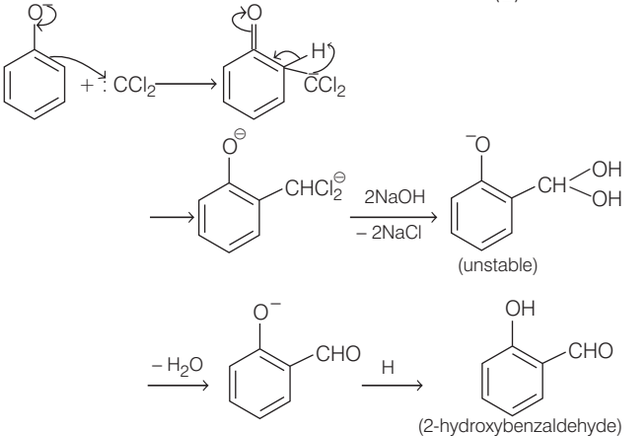
The electrophile involved in the above reaction is

(a) dichloromethyl cation $(\overset{\oplus}{C}HCl_2)$ **[AIEEE 2006]**
(b) dichlorocarbene $(:CCl_2)$
(c) trichloromethyl anion $(\overset{\ominus}{C}Cl_3)$
(d) formyl cation $(\overset{\oplus}{C}HO)$

Ans. ***(b)***



Dichloro carbene (*E*)



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55 Acid catalysed hydration of alkenes except ethene leads to the formation of **[AIEEE 2005]**

(a) mixture of secondary and tertiary alcohols
(b) mixture of primary and secondary alcohols
(c) secondary or tertiary alcohol
(d) primary alcohol

Ans. ***(c)***

Hydration of ethene gives 1° alcohol (ethanol) while all other alkenes give either 2° or 3° alcohols.

$$CH_2 = CH_2 \xrightarrow{H_2O/H^+} CH_3CH_2OH$$

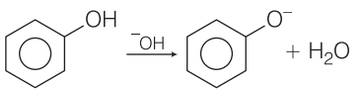
Ethene

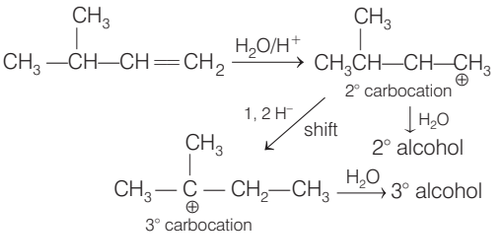
$$CH_3—CH = CH_2 \xrightarrow{H_2O/H^+} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

[(2°alcohol) through 2° carbocation $CH_3\overset{\oplus}{C}HCH_3$]

$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 \xrightarrow{H_2O/H^+} (CH_3)_3COH$$

[(3° alcohol) through 3° carbocation $(CH_3)_3\overset{\oplus}{C}$]





56 Among the following compounds which can be dehydrated very easily ? **[AIEEE 2004]**

(a) $CH_3CH_2CH_2CH_2CH_2OH$
(b) $CH_3CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$
(c) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_2CH_3$
(d) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2OH$

Ans. ***(c)***

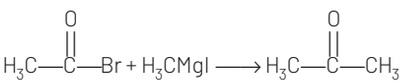
Dehydration of alcohol is in the order 1°< 2°< 3°

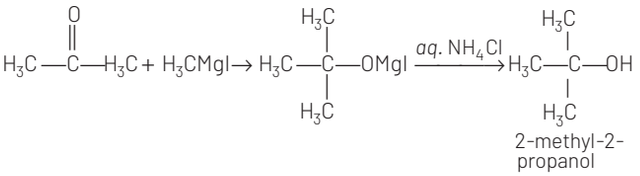
Thus (*c*), a 3° alcohol is dehydrated very easily.

57 Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives **[AIEEE 2004]**

(a) acetone
(b) acetamide
(c) 2-methyl-2-propanol
(d) acetyl iodide

Ans. ***(c)***





2-methyl-2-propanol

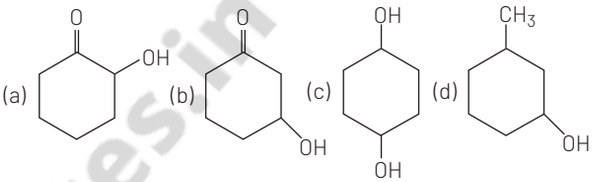
58 During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4 the initiation step is

(a) protonation of alcohol molecule **[AIEEE 2003]**
(b) formation of carbocation
(c) elimination of water
(d) formation of an ester

Ans. ***(a)***

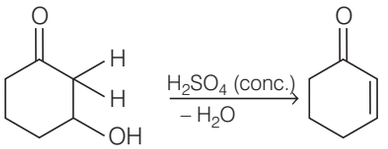
Protonation of —OH is first step. It involves conversion of poor leaving group (—OH) into good leaving group ($—\overset{+}{O}H_2$).

59 Maximum dehydration takes place in that of **[AIEEE 2002]**



Ans. ***(b)***

Dehydration takes place with the formation of more stable carbocation. Among the given compounds, only compound (b) forms conjugated carbocation. Thus, maximum amount of dehydration takes place in compound (*b*).



TOPIC 2
Ethers

60 Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Synthesis of ethyl phenyl ether may be achieved by Williamson synthesis.

Reason (R) Reaction of bromobenzene with sodium ethoxide yields ethyl phenyl ether.

In the light of the above statements, choose the most appropriate answer from the options given below **[2021, 27 Aug Shift-I]**

(a) Both (A) and (R) are correct and (R) is the correct explanation of (A)
(b) (A) is correct but (R) is incorrect
(c) (A) is incorrect but (R) is correct
(d) Both (A) and (R) are correct but (R) is not the correct explanation of (A)

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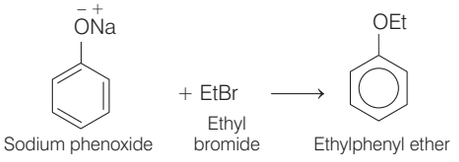
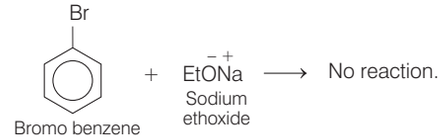
Ans. ***(b)***

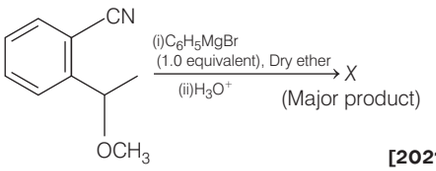
Williamson's synthesis is used to prepare mixed ethers as well as simple ether. To prepare ethyl phenyl ether following reaction take place.



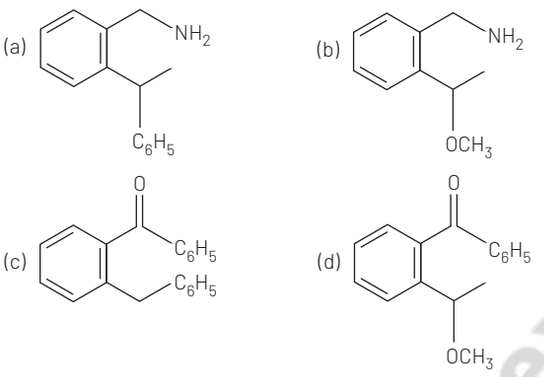


This reaction is not possible as bromine has partial double bond character with benzene ring, so it cannot be dissociated. So, Assertion is correct but Reason is not correct.

61

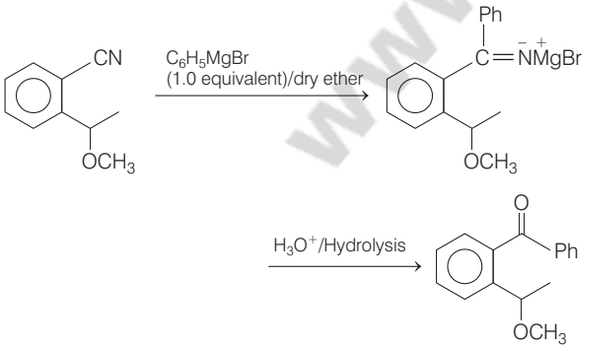


[2021, 16 March Shift-II]

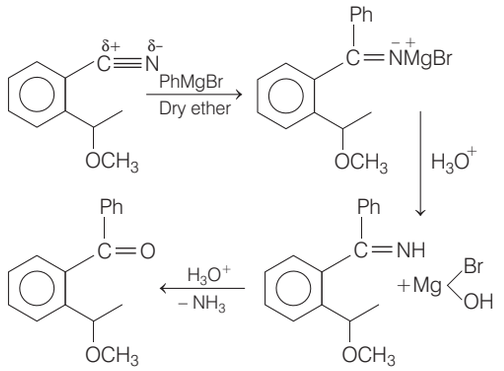


Ans. ***(d)***

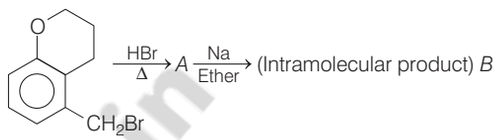
Cyanide undergoes nucleophilic addition with Grignard followed by hydrolysis to give carbonyl compound.

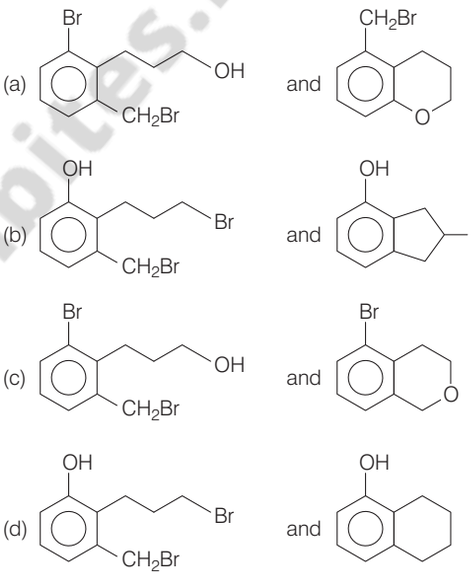


Mechanism Carbon of cyanide is electrophilic and is attacked by nucleophilic phenyl anion.



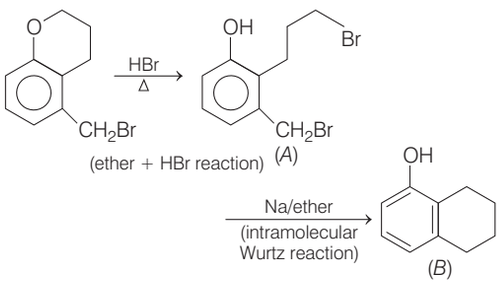
62 In the following reaction sequence, structures of *A* and *B*, respectively will be **[2020, 7 Jan Shift-II]**





Ans. ***(d)***

The given reaction can be completed as follows :



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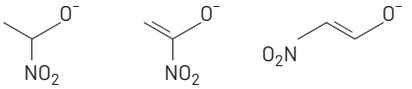
63 The correct order of stability for the following alkoxides is **[2020, 7 Jan Shift-II]**

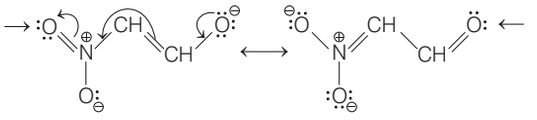


(A) (B) (C)

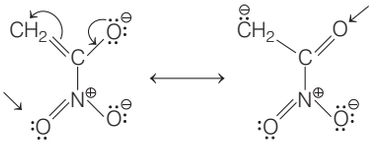
(a) (C) > (B) > (A) (b) (B) > (C) > (A)
(c) (B) > (A) > (C) (d) (C) > (A) > (B)

Ans. ***(a)***

(*C*) is most stable due to strong –*I* effect as well as –*R* (or –*M*) effect of '—NO_2' group. The negative charge is delocalised as represented by the following resonance structure :

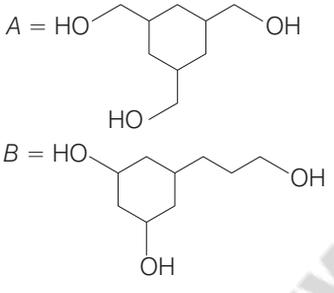


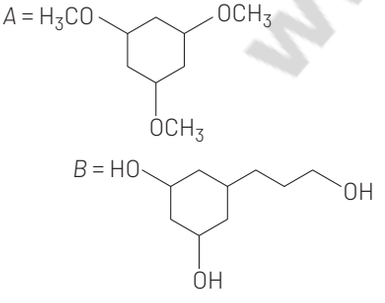
In (*A*), there is no resonance delocalisation of negative charge, and hence it is least stable. In (*B*), negative charge is delocalised by resonance as shown :

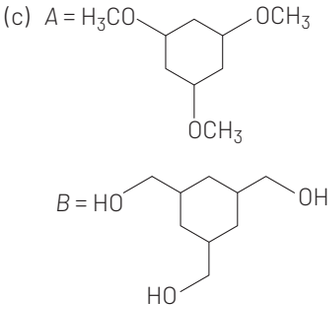


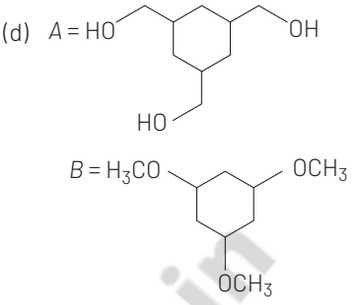
But the contribution of structure on RHS is relatively less, so stability of (*B*) is more than (*A*) but less than (*C*).

64 Among the compounds *A* and *B* with molecular formula $C_9H_{18}O_3$, *A* is having higher boiling point the *B*. The possible structures of *A* and *B* are **[2020, 8 Jan Shift-II]**

(a) 

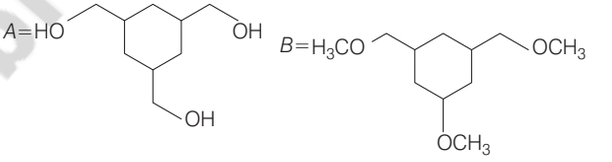
(b) 

(c) 

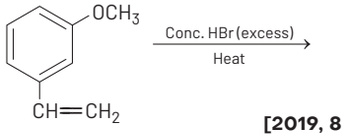
(d) 

Ans. ***(d)***

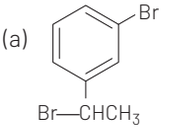
Alcohols have higher boiling point than ethers of same molecular mass due to possibility of intermolecular hydrogen bonds in alcohols and not in ethers. So, *A* is alcohol derivative and *B* is ether derivative.

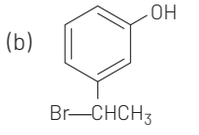


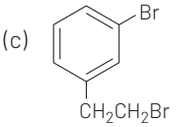
65 The major product of the following reaction is

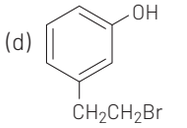


[2019, 8 April Shift-I]

(a) 

(b) 

(c) 

(d) 

Ans. ***(b)***

Key Idea Ethers are least reactive functional groups. The cleavage of C—O bond in ethers take place under drastic conditions with excess of H*X*.

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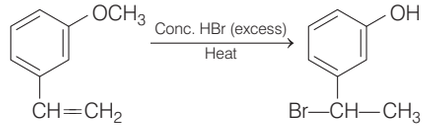
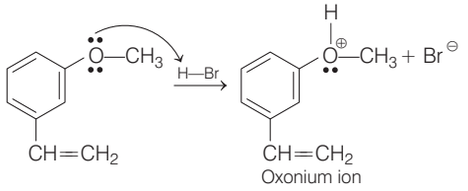
The major product obtained in the reaction is as follows:



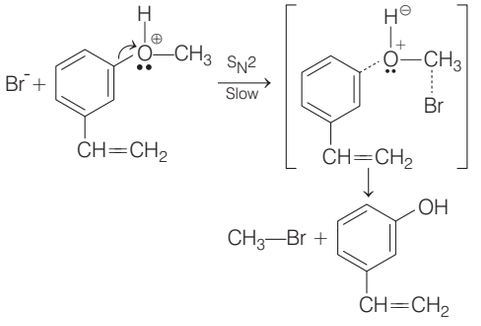
As conc. HBr is in excess. So, reaction will take place at both the substituents.

Mechanism

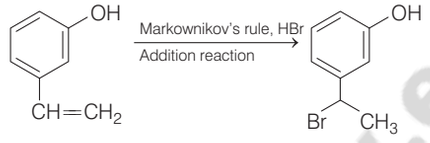
Step 1 Protonation of ether to form oxonium ion.



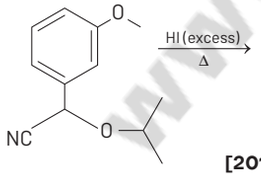
Step 2 Attack of nucleophile at the protonated ether.



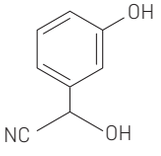
Step 3 As HBr is in excess, so, reaction will also take place at alkene.

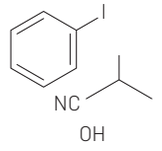


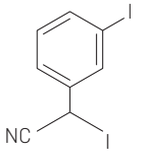
66 The major product of the following reaction is

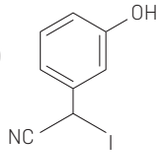


[2019, 10 April Shift-I]

(a) 

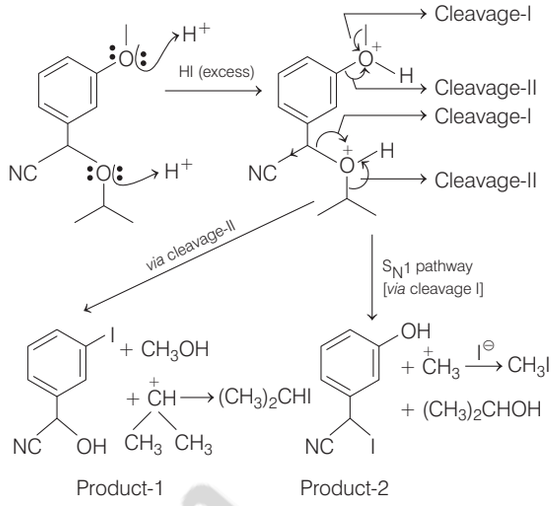
(b) 

(c) 

(d) 

Ans. ***(d)***

The given reaction takes place as follows :

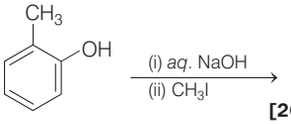


Product-2 is formed because

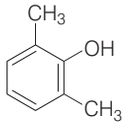
(i) Cleavage-I will give more stable aryl carbocation.

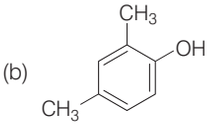
(ii) Cleavage- I will give intermediate which is in conjugation with ring.

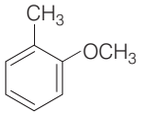
67 The major product of the following reaction is

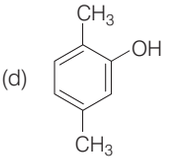


[2019, 10 Jan Shift-II]

(a) 

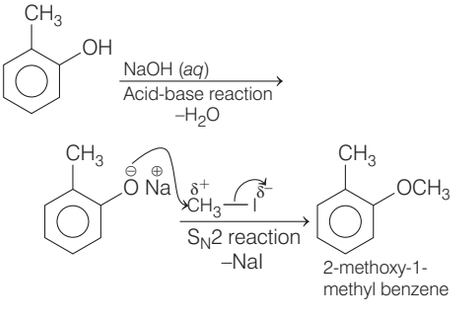
(b) 

(c) 

(d) 

Ans. ***(c)***

Substituted phenols react with *aq*. NaOH to form sodium phenoxides which on reaction with CH_3I undergoes S_N2 reaction to give 2-methoxy-1-methyl benzene.



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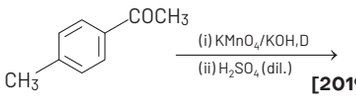
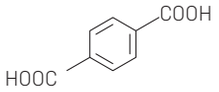
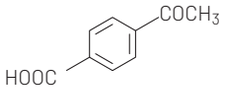
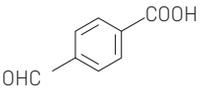
68 The major product of the following reaction is

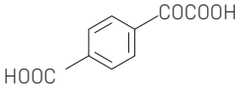


[2019, 11 Jan Shift-I]

(a) 

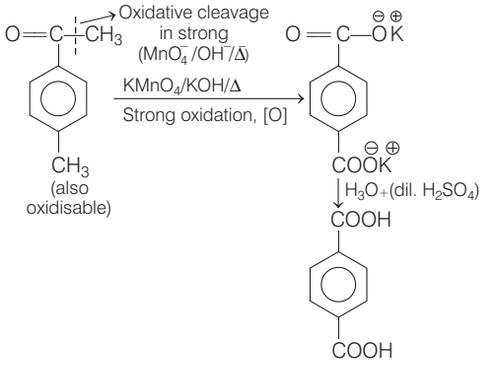
(b) 

(c) 

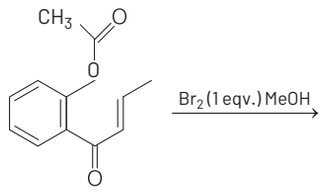
(d) 

Ans. ***(a)***

In presence of alkaline $KMnO_4$, vigorous oxidation of alkyl or acyl benzene takes place. During oxidation, aromatic nucleus remains intact but the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.



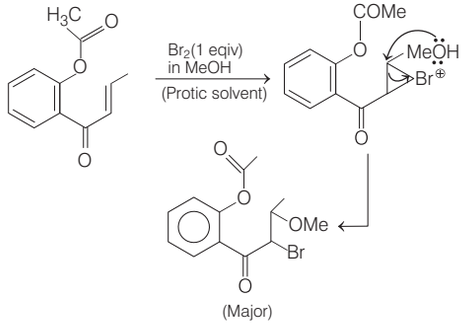
69 The major product obtained in the following conversion is



[2019, 11 Jan Shift-II]

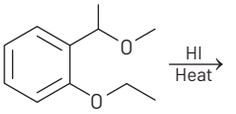
Ans. ***(b)***

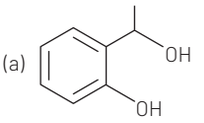
In presence of Br_2/EtOH, the reactant containing double bond undergoes electrophilic addition reaction *via* the formation of bromonium ion. On further attack of —$\ddot{O}$Me on bromonium ion gives the addition product.

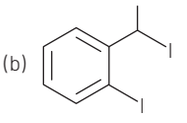


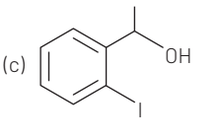
70 The major product formed in the following reaction is

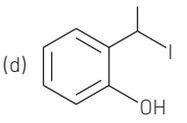
[JEE Main 2018]



(a) 

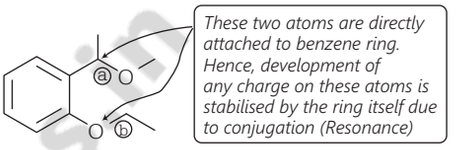
(b) 

(c) 

(d) 

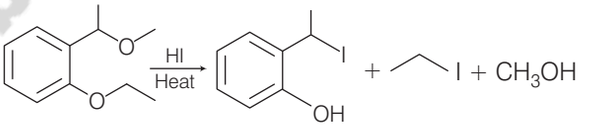
Ans. ***(d)***

The reaction given is a nucleophilic substitution reaction in which cleavage at C—O bond is visible. The product formation can be visualised with the help of following analysis.



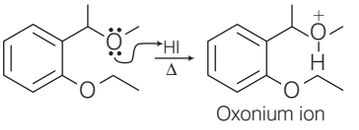
If any one properly visualise the fact written with figure above, than a conclusion can be made that C—O bonds marked (a) and (b) in the figure will undergo heterolysis during the reaction.

The reaction can be represented as



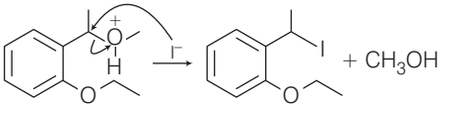
Mechanism

Step I The reaction begins with the attack of H^+ of HI on oxygen to form oxonium ion as

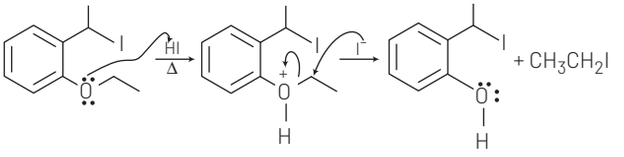


Oxonium ion

Step II This oxonium ion undergoes lysis and addition of I^- to form two products as



Step III Similar pathway is followed at the other oxygen atom, which can be visualised as



Note Mechanism of a reaction is always a logical sequencing of events which may occur simultaneously as well.

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71 Consider the following reaction,

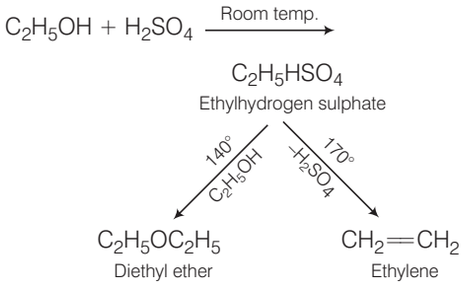
$$C_2H_5OH + H_2SO_4 \longrightarrow \text{Product}$$

Among the following, which one cannot be formed as a product under any conditions? **[AIEEE 2011]**

(a) Ethyl hydrogen sulphate (b) Ethylene
(c) Acetylene (d) Diethyl ether

Ans. ***(c)***

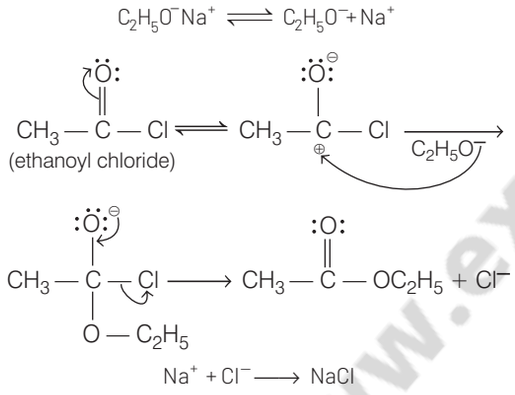
(a), (b), (d) may be formed but (c) is never formed.



72 Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is **[AIEEE 2011]**

(a) diethyl ether (b) 2-butanone
(c) ethyl chloride (d) ethyl ethanoate

Ans. ***(d)***



This is by S_N reaction. Cl^- is a better leaving group than $C_2H_5O^-$ and the ethyl ethanoate is formed.

73 An ether is more volatile than an alcohol having the same molecular formula. This is due to **[AIEEE 2003]**

(a) dipolar character of ethers
(b) alcohols having resonance structures
(c) intermolecular hydrogen bonding in ethers
(d) intermolecular hydrogen bonding in alcohols

Ans. ***(d)***

Alcohol has polar H which makes intermolecular H-bonding possible. Ether is non-polar, hence has no H-bonding. Lack of H-bonding in ether makes it more volatile than alcohol.

TOPIC 3
Aldehydes and Ketones

74 Given below are two statements.

Statement I The nucleophilic addition of sodium hydrogen sulphite to an aldehyde or a ketone involves proton transfer to form a stable ion.

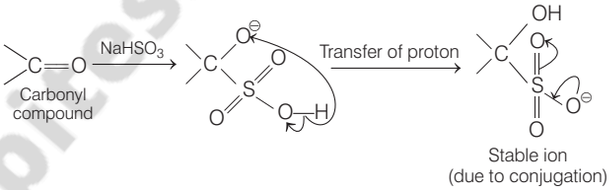
Statement II The nucleophilic addition of hydrogen cyanide to an aldehyde or a ketone yields amine as final product.

In the light of the above statements, choose the most appropriate answer from the options given below. **[2021, 1 Sep Shift-II]**

(a) Both statement I and statement II are true.
(b) Statement I is false but statement II is true.
(c) Statement I is true but statement II is false.
(d) Both statement I and statement II are false.

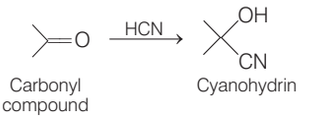
Ans. ***(c)***

Nucleophilic addition of sodium hydrogen sulphite ($NaHSO_3$) to carbonyl compound (aldehyde or ketone) involves proton transfer to form a stable ion.



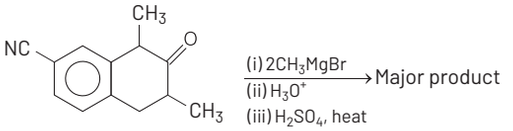
Hence, statement I is true.

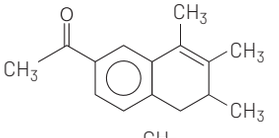
Nucleophilic addition of HCN (hydrogen cyanide) to an aldehyde/ketone yield cyanohydrin as final product.

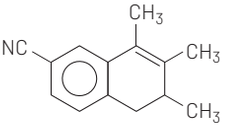


Hence, statement II is false.

75 Which one of the following is the major product of the given reaction? **[2021, 27 Aug Shift-II]**



(a) 

(b) 

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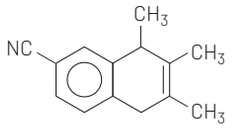
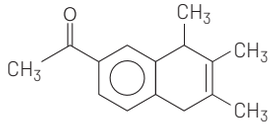
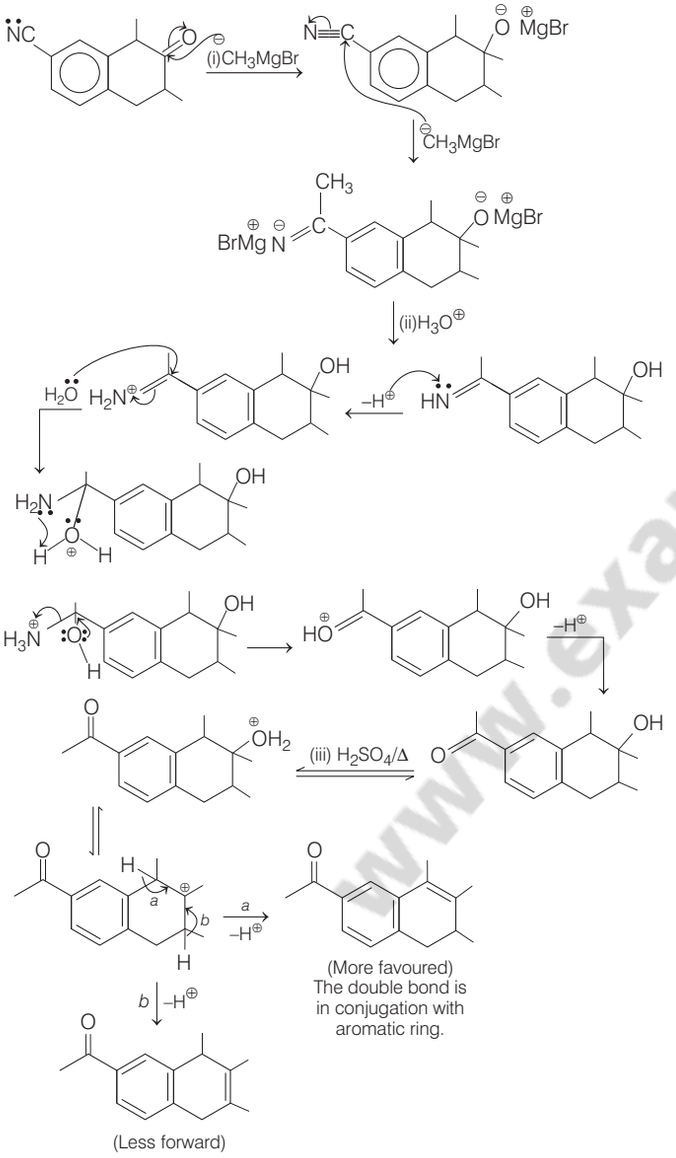
(c) 

(d) 

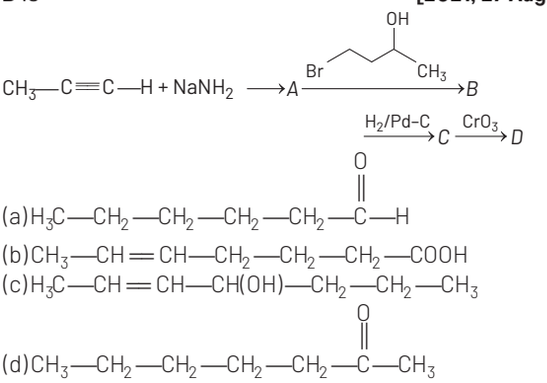
Ans. ***(a)***

The reaction of keto and cyanide group with Grignard reagent and further hydrolysis gives alcohol and keto group respectively. On further heating with H_2SO_4 at — OH group is eliminated resulting in formation of alkene.



Therefore, option (a) is correct.

76 In the following sequence of reactions, the final product *D* is **[2021, 27 Aug Shift-I]**



(a) $H_3C—CH_2—CH_2—CH_2—CH_2—\overset{O}{\overset{\|}{C}}—H$

(b) $CH_3—CH=CH—CH_2—CH_2—CH_2—COOH$

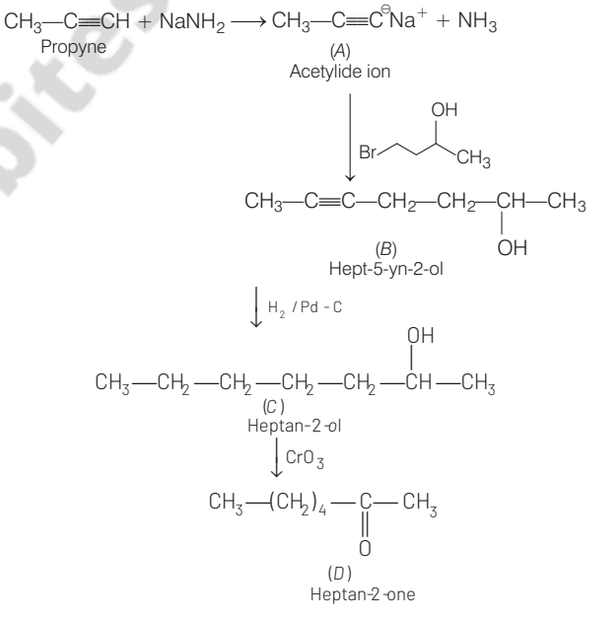
(c) $H_3C—CH=CH—CH(OH)—CH_2—CH_2—CH_3$

(d) $CH_3—CH_2—CH_2—CH_2—CH_2—\overset{O}{\overset{\|}{C}}—CH_3$

Ans. ***(d)***

$NaNH_2$ is a strong base that causes deprotonation of propyne and forms acetylide ion (*A*) which further combines with the carbon chain and forms hept-5-yn-2-ol (*B*) that undergoes reduction in presence of H_2/Pd-C and forms heptan-2-ol (*C*). Being a secondary alcohol *(C)*, oxidises in presence of CrO_3 to give corresponding ketone i.e. heptan-2-one (*D*).

The complete reaction take place as follows.



77 $R—CN \xrightarrow[(ii)\,H_2O]{(i)\,DIBAL\text{-}H} R—Y$

Consider the above reaction and identify *Y*. **[2021, 27 July Shift-II]**

(a) $—CH_2NH_2$ (b) $—CONH_2$ (c) — CHO (d) — COOH

Ans. ***(c)***

DIBAL-H, i.e. di-isobutyl aluminium hydride causes partial reduction of cyanide group and further hydrolysis forms corresponding aldehyde.

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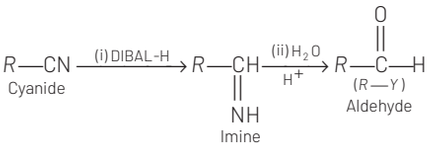
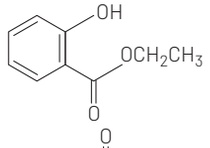
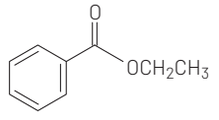
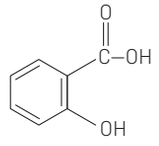


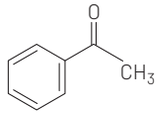
Hence, *Y* is —CHO group.

78 Which one of the following compounds will give orange precipitate when treated with 2, 4 dinitrophenyl hydrazine? **[2021, 27 July Shift-I]**

(a) 

(b) 

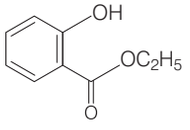
(c) 

(d) 

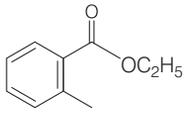
Ans. ***(d)***

2, 4-dinitrophenylhydrazine can be used for qualitative identification of ketone or aldehyde functional group.

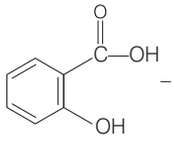
A successful test is indicated by formation of yellow, orange or red colour precipitate which is known as dinitrophenylhydrazone.

(a) 

– Presence of alcohol and ester

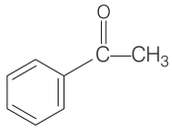
(b) 

– Presence of ester group

(c) 

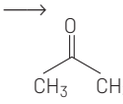
– Presence of alcoholic and carboxylic acid group

Above compounds will not give 2, 4-DNP test due to absence of carbonyl group.

(d) 

– Presence of ketone group, so it will give orange ppt. when treated with 2, 4-DNP.

79 Match List-I with List-II.

	List-I (Chemical reaction)		**List-II** (Reagent used)
A.	$CH_3COOC_2H_5 \longrightarrow C_2H_5OH$	1.	CH_3MgBr/H_3O^+ (1.equivalent)
B.	$CH_3COOCH_3 \longrightarrow CH_3CHO$	2.	H_2SO_4/H_2O
C.	$CH_3C\equiv N \longrightarrow CH_3CHO$	3.	DIBAL - H/H_2O
D.	$CH_3C\equiv N \longrightarrow$ 	4.	$SnCl_2$, HCl/H_2O

Choose the most appropriate option given below. **[2021, 26 Aug Shift-II]**

	A	B	C	D
(a)	2	4	3	1
(c)	2	3	4	1

	A	B	C	D
(b)	4	2	3	1
(d)	3	2	1	4

Ans. ***(c)***

(A) This reaction is reverse of esterification. As it takes place in presence of acid and the ester molecule gets hydrolysed, the reaction is called as acidic hydrolysis of ester (hydrolysis is breaking of molecule in presence of water). Acidic hydrolysis is reversible reacton, hence does not go to completion.

$$\underset{\text{Ester}}{CH_3COOC_2H_5} \xrightarrow[H_2O]{H_2SO_4} \underset{\text{Alcohol}}{C_2H_5OH}$$

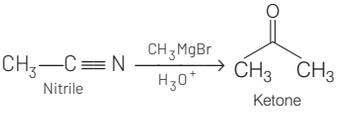
(B) Diisobutylaluminium hydride (DIBAL-H) is a reducing agent, which reduces ester to aldehyde.

$$\underset{\text{Ester}}{CH_3COOCH_3} \xrightarrow[H_2O]{\text{DIBAL-H}} \underset{\text{Aldehyde}}{CH_3CHO}$$

(C) This reaction is called Stephen aldehyde synthesis which involves preparation of aldehyde from nitrile using $SnCl_2$, HCl and quenching of resulting iminium salt ($[R\text{-}CH=NH_2]^+Cl^-$) with H_2O.

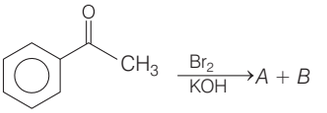
$$\underset{\text{Nitrile}}{CH_3C\equiv N} \xrightarrow[HCl/H_2O]{SnCl_2} \underset{\text{Aldehyde}}{CH_3CHO}$$

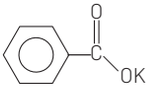
(D) Grignard reagent (CH_3MgBr) attack electrophilic carbon in the nitrile to form imine salt, this salt then gets hydrolysed to form a ketone.



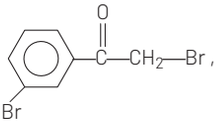
Thus, the correct match is (c) $A \to 2$, $B \to 3$, $C \to 4$, $D \to 1$.

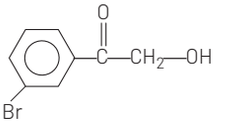
80 The major products formed in the following reaction sequence *A* and *B* are **[2021, 26 Aug Shift-I]**



(a) *A*= 

, *B*=$CHBr_3$

(b) *A*= 

, *B*= 

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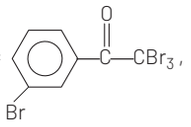
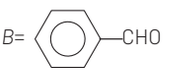
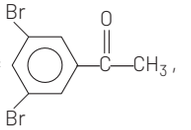
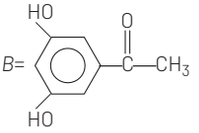
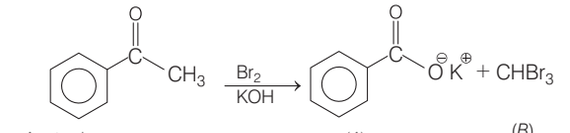
(c) *A*=  , *B*= 

(d) *A*=  , *B*= 

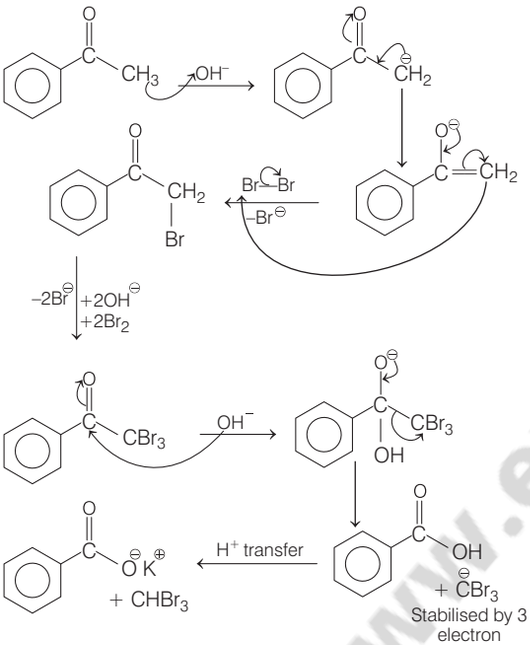
Ans. ***(a)***

Acetophenone is a methyl ketone which on reaction with Br_2 and KOH will give conjugate base of an acid and methyl group will turn into haloform. This reaction is haloform reaction.



Acetophenone (*A*) Conjugate base of acid (*B*) Haloform (Bromoform)

Mechanism

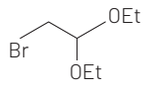
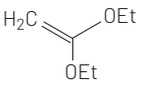


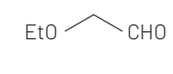
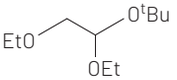
Stabilised by 3 electron withdrawing groups

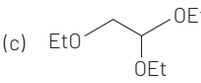
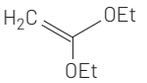
81

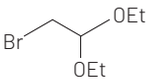
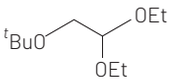
[where, $Et = C_2H_5$, $^tBu = (CH_3)_3C-$]

Consider the above reaction sequence, product *A* and product *B* formed respectively are **[2021, 25 July Shift-II]**

(a)  , 

(b)  , 

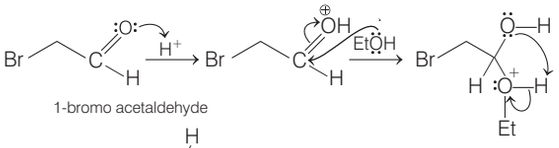
(c)  , 

(d)  , 

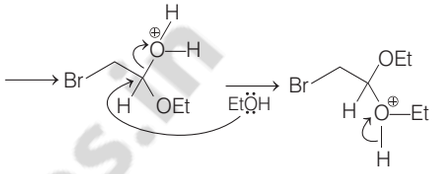
Ans. ***(a)***

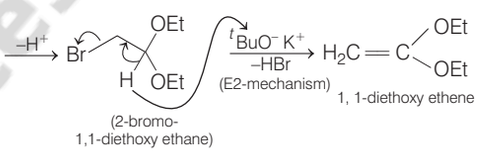
In reaction *t*-$BuO^{\ominus}H^+$ is used as a base to remove HBr and form alkene as a major product (*B*) *via* E2 elimination mechanism.

Machanism Firstly, 1-bromoacetaldehyde undergoes protonation which is then react with *t*-$BuO^{\ominus}H^+$. (*t*- $BuO^{\ominus}$ act as nucleophile and attack on carbonyl carbon). In next step, *t*-$BuO^{\ominus}H^+$ act as base and accepts proton and at last alkene is formed as major product.



1-bromo acetaldehyde





(2-bromo-1,1-diethoxy ethane) (E2-mechanism) 1, 1-diethoxy ethene

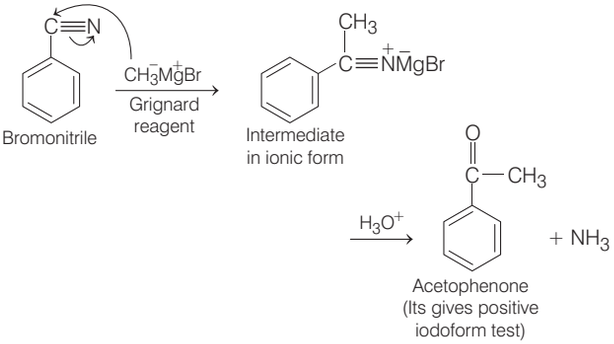
82 A reaction of benzonitrile with one equivalent CH_3MgBr followed by hydrolysis produces a yellow liquid *P*. The compound *P* will give positive **[2021 25 July Shift-II]**

(a) iodoform test (b) Schiff's test

(c) ninhydrin's test (d) Tollen's test

Ans. ***(a)***

Treatment of benzonitrile with Grignard reagent followed by acid hydrolysis gives acetophenone product.



Bromonitrile Grignard reagent Intermediate in ionic form Acetophenone (Its gives positive iodoform test)

Iodoform test is used to check the presence of carbonyl compound with the structure *R*—CO—CH_3 or alcohols with the structure *R*—CH(OH)—CH_3 in a given unknown substance. The reaction of iodine, a base and a methyl ketone gives a yellow precipitate along with an "antiseptic" smell.

$$C_6H_5—CO—CH_3 + I_2 + NaOH \longrightarrow C_6H_5COONa + CHI_3 \downarrow$$

This conclude that acetophenone give iodof form test.

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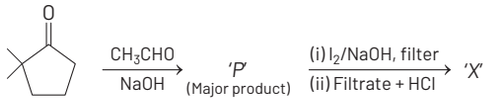
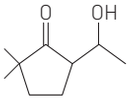
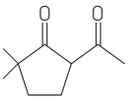
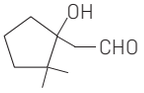
83 

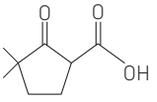
Consider the given reaction, the product *X* is

[2021, 22 July Shift-I]

(a) 

(b) 

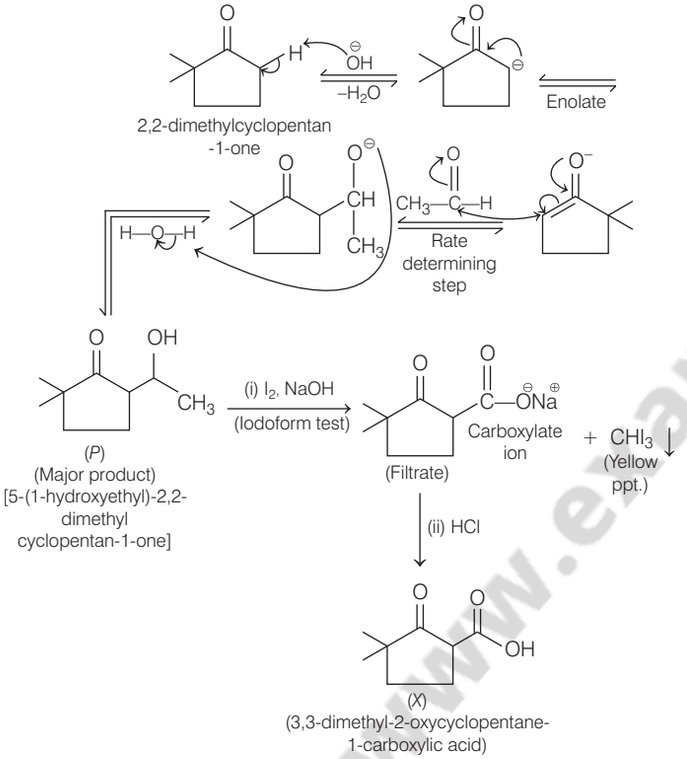
(c) 

(d) 

Ans. ***(d)***

In first step, aldol reaction is involved in reaction mechanism and in second step, (I_2, NaOH) is used for iodoform test, which gives CHI_3 (yellow precipitate) as by product.

Reaction Mechanism

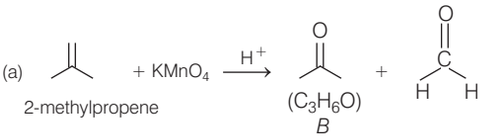


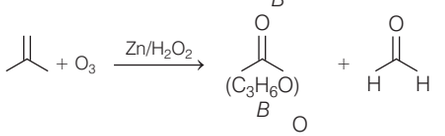
84 An organic compound '*A*' C_4H_8 on treatment with $KMnO_4$ /H^+ yield's compound '*B*' C_3H_6O.
Compound '*A*' also yields compound '*B*' an ozonolysis.
Compound '*A*' is **[2021, 25 July Shift-I]**

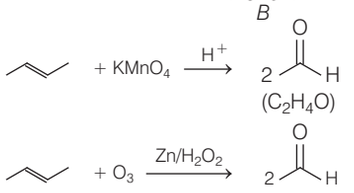
(a) 2-methylpropene
(b) 1-methylcyclopropane
(c) but-2-ene
(c) cyclobutane

Ans. ***(a)***

Alkenes react with $KMnO_4$ / H^+ and O_3 to give carbonyl compound.

(a) 



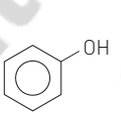
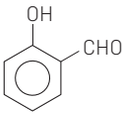
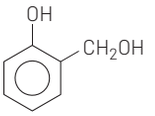
(c) 

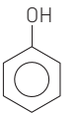
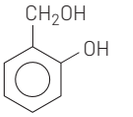
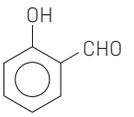
So, only 2-methylpropene gives compound *B* with molecular formula, C_3H_6O.

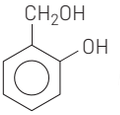
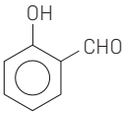
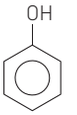
Therefore, compound *A* is 2-methylpropene.

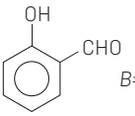
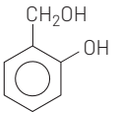
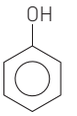
85 An organic compound *A* (C_6H_6O) gives dark green colouration with ferric chloride. On treatment with $CHCl_3$ and KOH, followed by acidification gives compound *B*. Compound *B* can also be obtained from compound *C* on reaction with pyridinium chlorochromate (PCC). Identify *A*, *B* and C.

[2021, 22 July Shift-II]

(a) *A*=  *B*=  *C*= 

(b) *A*=  *B*=  *C*= 

(c) *A*=  *B*=  *C*= 

(d) *A*=  *B*=  *C*= 

Ans. ***(a)***

Compound *A* is phenol, compound *B* is salicylaldehyde and compound *C* is 2-hydroxy methyl phenol.

When phenols react with ferric chloride solution to give blue, violet or green colouration due to the formation of ferric phenoxide which gives different coloured water soluble complex compounds.

Phenol reacts with chloroform and alcoholic KOH to give salicylaldehyde. This reaction is called Reimer-Tiemann reaction.

Salicylaldehyde also obtained on reaction of 2-hydroxy methyl phenol with pyridinium chlorochromate (PCC).

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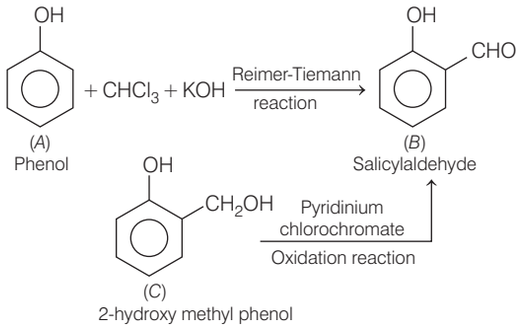
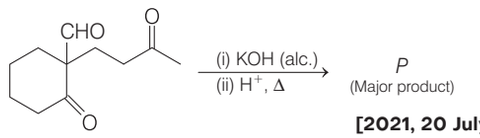
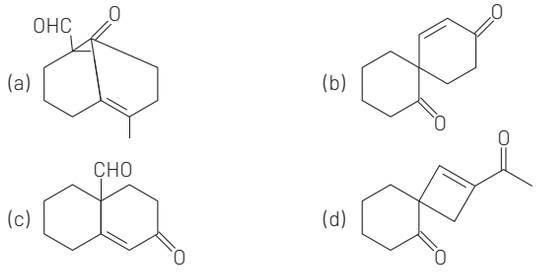
Chemical reactions are as follows :



86 The major product *P* in the following reaction is

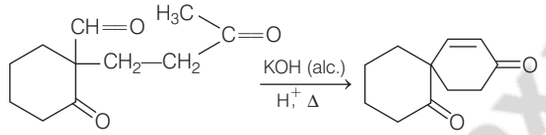


[2021, 20 July Shift-II]



Ans. ***(b)***

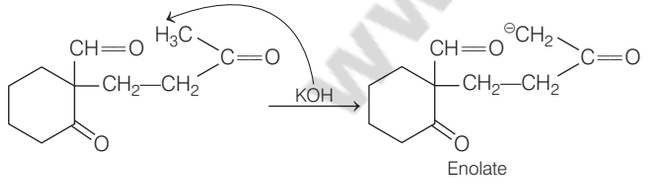
Given reaction is aldol condensation.



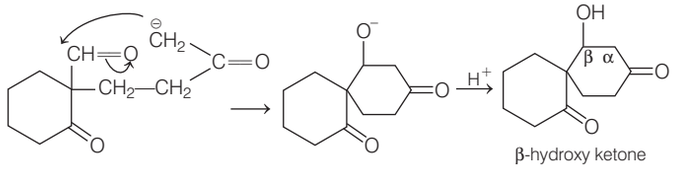
In this reaction, substrate undergoes intramolecular aldol condensation in which condensation reaction of two aldehyde groups or ketone groups occur in same molecule.

Mechanism

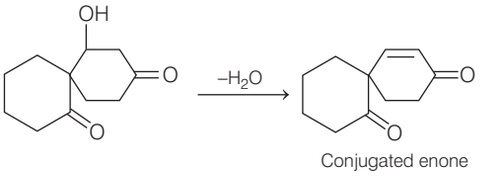
Step I Abstraction of proton by base KOH to form enolate.



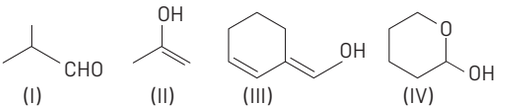
Step II Reaction of enolate and aldehyde group on substrate to form β-hydroxy ketone.



Step III β-hydroxy ketone undergoes dehydrate to form a conjugated enone.



87



Which among the above compound/s does/do not form silver mirror when treated with Tollen's reagent?

[2021, 20 July Shift-I]

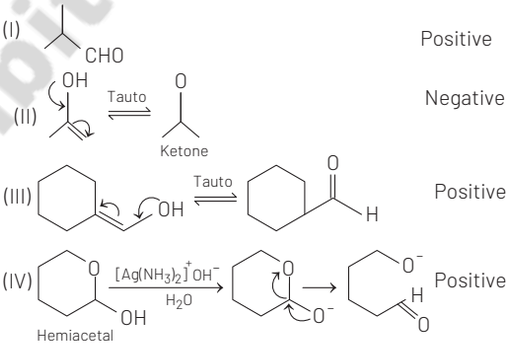
(a) (I), (III) and (IV) only (b) Only (IV)
(c) Only (II) (d) (III) and (IV) only

Ans. ***(c)***

Only compound (II) which has ketonic group does not form silver mirror when treated with Tollen's reagent.

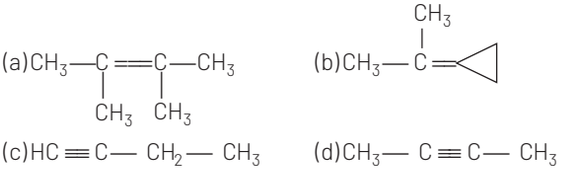
Because Tollen's reagent oxidises an aldehyde into the corresponding carboxylic acid. Ketones are not oxidised by Tollen's reagent, so the treatment of a ketone with Tollen's reagent in a glass test tube does not result in a silver mirror.

Aldehydes give positive Tollen's test (silver mirror test).



88 An unsaturated hydrocarbon *X* on ozonolysis gives *A*. Compound *A* when warmed with ammonical silver nitrate forms a bright silver mirror along the sides of the test tube. The unsaturated hydrocarbon *X* is

[2021, 17 March Shift-II]



Ans. ***(c)***

On ozonolysis, unsaturated hydrocarbon *X* will form carbonyl compound, which gives positive Tollen's test. So, it should be aldehyde.

(a) 2, 3-dimethylbut-2-ene undergoes ozonolysis reaction to give 2 molecules of acetone.

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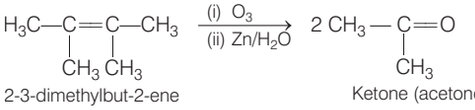
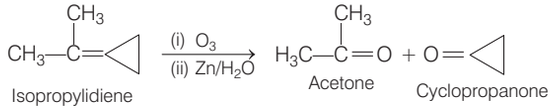
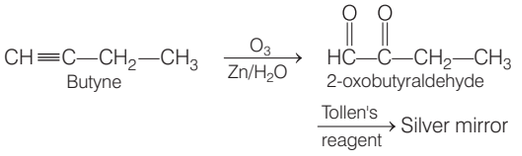


(b) Isopropylidiene undergoes ozonolysis reaction to give acetone along with cyclopropanone.

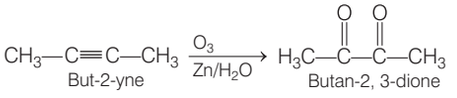


(c) Butyne reacts with O_3 and Zn/H_2O to give 2-oxobutyraldehyde. The aldehyde will give Tollen's test to give silver mirror.

Note Tollen's reagent contain silver nitrate ($AgNO_3$), ammonia and sodium hydroxide (NaOH) which react with aldehydes to give Ag (silver mirror).

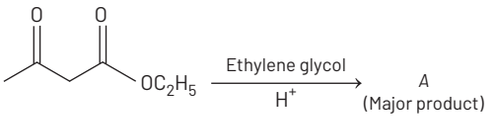


(d) But-2-yne undergoes ozonolysis to give butan-2, 3-dione.



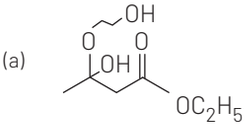
Only product of option (c) contains aldehyde group.

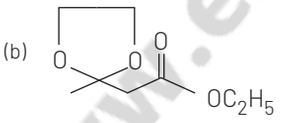
89

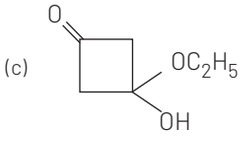


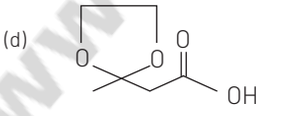
The product in the above reaction is

[2021, 16 March Shift-I]

(a) 

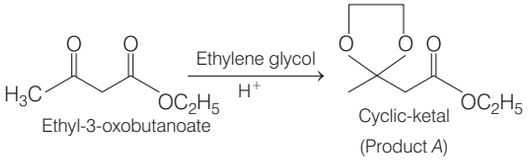
(b) 

(c) 

(d) 

Ans. ***(b)***

Nucleophilic addition of ethylene glycol in ketone to give ketal.



Addition of one molecule of alcohol on ketone give hemiketal and addition of two molecules give ketal.

90 **Assertion (A)** Enol form of acetone $[CH_3COCH_3]$ exists in < 0.1% quantity. However, the enol form of acetyl acetone $[CH_3COCH_2OCCH_3]$ exists in approximately 15% quantity.

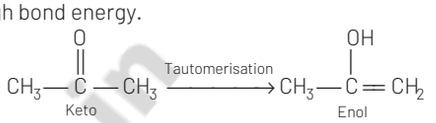
Reason (R) Enol form of acetyl acetone is stabilised by intramolecular hydrogen bonding, which is not possible in enol form of acetone.

Choose the correct statement. **[2021, 16 March Shift-I]**

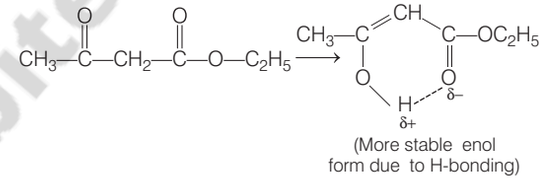
(a) A is false but R is true.
(b) Both A and R are true and R is the correct explanation of A.
(c) Both A and R are true but R is not the correct explanation of A.
(d) A is true but R is false.

Ans. ***(b)***

Enol form of acetone $[CH_3COCH_3]$ exists in < 0.1% quantity as monocarbonyl are more stable in keto form due to high bond energy.

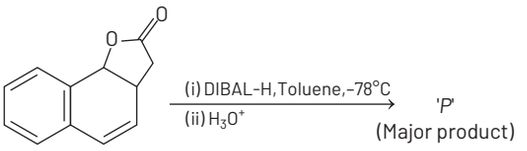


The enol form of acetyl acetone $[CH_3COCH_2OCCH_3]$ exists in approximately 15% quantity as it is stabilised by intramolecular hydrogen bonding, which is not possible in enol form of acetone.



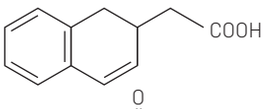
So, both A and R are true and R is the correct explanation of A.

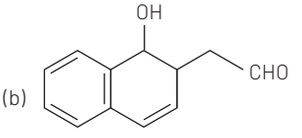
91

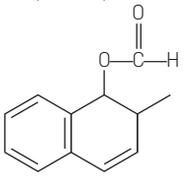


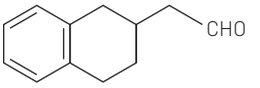
The product *P* in the above reaction is

[2021, 16 March Shift-I]

(a) 

(b) 

(c) 

(d) 

Ans. ***(b)***

DIBAIL is added to produce aldehyde from ester by keeping the temperature low while at higher temperature it can perform different conversions.

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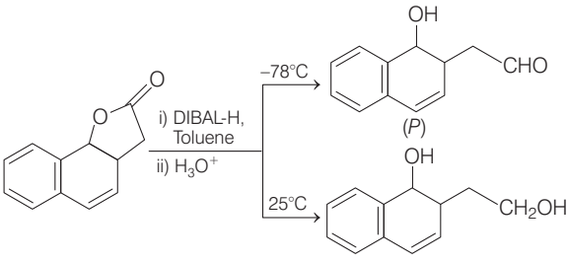
Complete reaction is as follows:



Diisobutyl aluminium hydride (DIBAL-H) is parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.

It forms different product at different temperature.

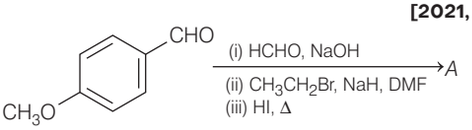
Role of DIBAL-H is shown below

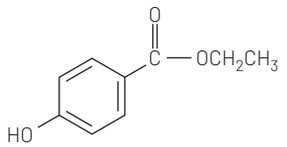
Reagent	**DIBAL-H** (– 78°C)	**DIBAL-H** (25° C)	**DIBAL-H** (–78°C)
Reactant	Ester	Ester	Cyanide
Product	Aldehyde	Alcohol	Aldehyde

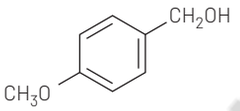
Note : DIBAL-H does not reduce double bond.

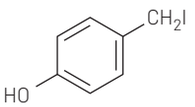
92 Identify *A* in the following chemical reaction.

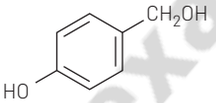
[2021, 26 Feb Shift-II]



(a) 

(b) 

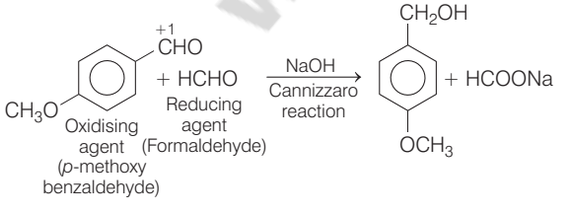
(c) 

(d) 

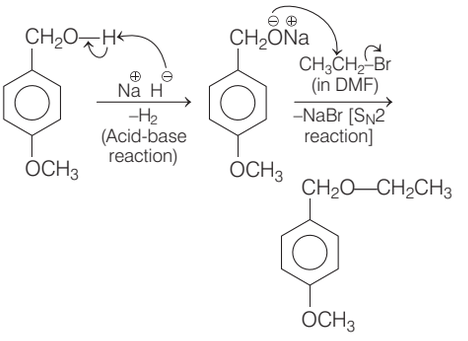
Ans. ***(c)***

Here, 4-methoxybenzaldehyde in series of reaction finally forms 4-(iodomethyl) phenol (*A*). Let us compute the reaction step by step with mechanism as follows

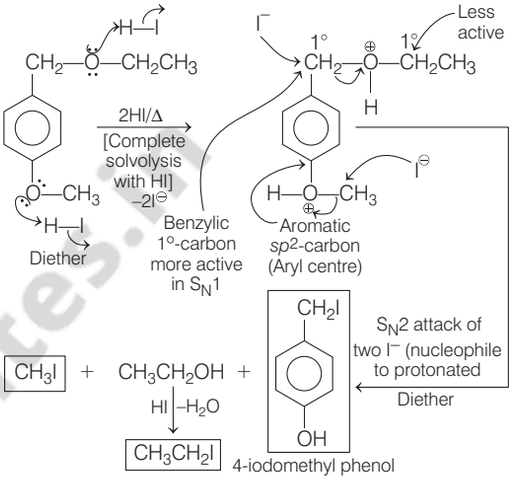
(i) In first step, oxidising agent (*p*-methoxybenzaldehyde) reacts with formaldehyde in presence of strong base NaOH to give *p*-methoxybenzyl alcohol along with sodium salt of methanoic acid. It is known as Cannizzaro's reaction.



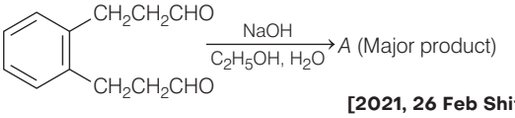
(ii) In second step, deprotonation of *p*-methoxybenzyl alcohol in presence of sodium hydride (NaH) to form alkoxide which further react with bromoethane in presence of DMF to give 1-ethoxymethyl-4-methoxybenzene.



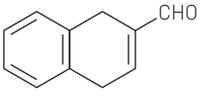
(iii) In last step, 1-ethoxymethyl-4-methoxybenzene undergoes solvolysis reaction followed by S_N2 attack of two iodide ion (I^-) to give 4-iodomethyl phenol, iodoform and iodoethane.

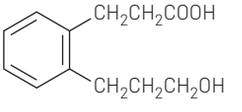


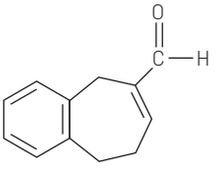
93 Identify *A* in the given chemical reaction,

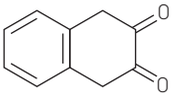


[2021, 26 Feb Shift-II]

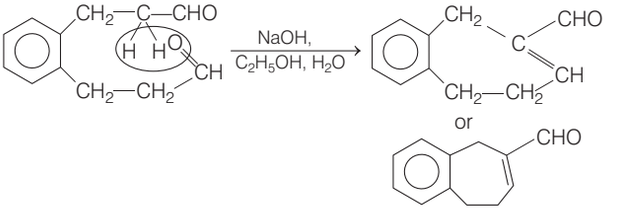
(a) 

(b) 

(c) 

(d) 

Ans. ***(c)***



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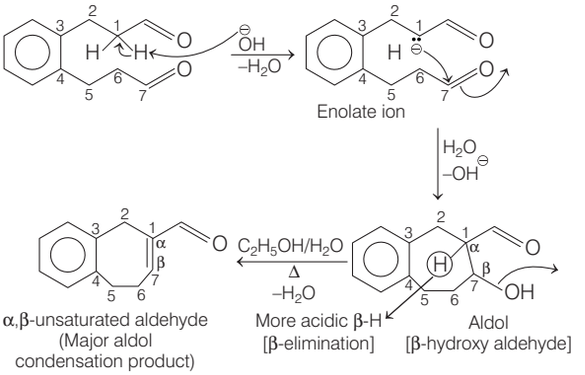
It is an example of intramolecular aldol condensation.
α - hydrogen atom of one — CHO group gets abstracted by NaOH form enolate ion which then attacks of another — CHO group to form aldol or β - hydroxy aldehyde. The aldol on heating C_2H_5OH/H_2O forms the final product (α, β-unsaturated aldehyde) as the major product.

Mechanism

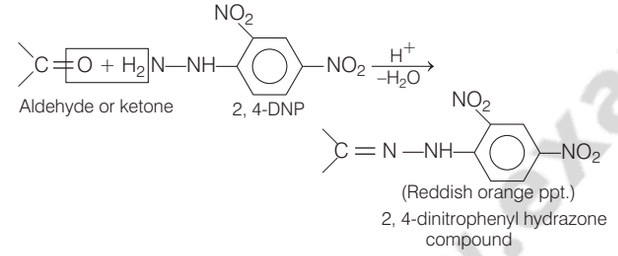


94 2,4-DNP test can be used to identify **[2021, 26 Feb Shift-II]**

(a) amine (b) aldehyde
(c) ether (d) halogens

Ans. ***(b)***

2, 4 - DNP test is used to detect the presence of carbonyl group (aldehyde or ketone) in organic compound. The test is carried out with 2, 4- dinitro phenyl hydrazine or 2, 4 - DNP (Brady's reagent) to give a reddish orange precipitate.



95 $A \xrightarrow[373\ K]{\text{Hydrolysis}} B$
$(C_4H_8Cl_2)$ (C_4H_8O)

B reacts with hydroxyl amine but does not give Tollen's test. Identify *A* and *B*. **[2021, 26 Feb Shift-I]**

(a) 1,1-dichlorobutane and 2-butanone
(b) 2,2-dichlorobutane and butanal
(c) 1,1-dichlorobutane and butanal
(d) 2,2-dichlorobutane and 2-butan-one

Ans. ***(d)***

Compound *B* (C_4H_8O) reacts with hydroxylamine (NH_2OH). So, compound *B* is an aldehyde or a ketone. Again, *B* does not give Tollen's test which indicates that *B* is a ketone but not an aldehyde. So, *B* is

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$ (C_4H_8O)
2-butan-one

Compound *A* ($C_4H_8Cl_2$) is a dihalide which undergoes hot hydrolysis (H_2O/373 K) to give *B*, a ketone. So, *A* is a non-terminal *geminal* or *gem* dichloride and *A* is

$CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_2CH_3$ $(C_4H_8Cl_2)$
2,2-dichlorobutane

The reaction can be computed as,

$CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_2CH_3 \xrightarrow[-2HCl]{2H_2O/373K} CH_3-\overset{OH}{\underset{Cl}{C}}-CH_2CH_3 \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$
(*A*) 2, 2-dichlorobutane
Butane-2, 2-diol (unstable) [Non-terminal *gem*-diol]
(*B*) 2-butanone

96 The major product of the following reaction is

$CH_3CH_2CH=CH_2 \xrightarrow[\text{Rh catalyst}]{H_2/CO}$ **[2021, 25 Feb Shift-II]**

(a) $CH_3CH_2CH_2CH_2CHO$ (b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2CH=CH-CHO$ (d) $CH_3CH_2\underset{\underset{CHO}{|}}{C}=CH_2$

Ans. ***(a)***

The major product of the reaction is $CH_3CH_2CH_2CH_2CHO$. Here, electrophilic addition of $H-\overset{+}{C}=O$ (formylation) take place to the alkene through Markownikoff addition.

(i) $H_2 + :C\equiv O: \xrightarrow[\text{(Catalyst)}]{Rh} [H-\overset{\oplus}{C}=O]H^S$
Water gas

(ii) $CH_3CH_2-CH=CH_2 \xrightarrow[\text{Slow}]{H-\overset{\oplus}{C}=O} CH_3CH_2-\overset{\oplus}{C}H-CH_2-CHO \xrightarrow[\text{Fast}]{H^\ominus} CH_3CH_2CH_2CH_2CHO$ (major)
But-1-ene Pentanal

97 Which one of the following reactions will not form acetaldehyde? **[2021, 25 Feb Shift-I]**

(a) $CH_2=CH_2 + O_2 \xrightarrow[H_2O]{Pd(II)/Cu(II)}$

(b) $CH_3CH_2OH \xrightarrow{CrO_3\text{-}H_2SO_4}$

(c) $CH_3CN \xrightarrow[(ii)\,H_2O]{(i)\,DIBAL\text{-}H}$

(d) $CH_3CH_2OH \xrightarrow[573\ K]{Cu}$

Ans. ***(b)***

$CH_2=CH_2 + O_2 \xrightarrow[H_2O]{Pd(II)/Cu(II)} CH_3CHO$
Ethene Ethanal

$CH_3CH_2OH \xrightarrow{CrO_3\cdot H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH$
Ethanol Ethanoic acid

$CH_3CN \xrightarrow[H_2O]{DIBAL\text{-}H} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[573\ K]{CH_3CH_2OH,\ Cu} CH_3CHO$
Acetonitrile Ethanal Ethanol Ethanal

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Since, $CrO_3 \cdot H_2SO_4$ behave as strong oxidising agent and it converts alcohol directly to carboxylic acid. Thus, reaction (b) will not form acetaldehyde.

98 The major product of the following chemical reaction is

$$CH_3CH_2CN \xrightarrow[(iii)\,Pd/BaSO_4,\,H_2]{(i)\,H_3O^+,\,\Delta \;\; (ii)\,SOCl_2} ?$$

[2021, 25 Feb Shift-I]

(a) $CH_3CH_2CH_2OH$ (b) $(CH_3CH_2CO)_2O$
(c) $CH_3CH_2CH_3$ (d) CH_3CH_2CHO

Ans. ***(d)***

The complete reaction take place as follows

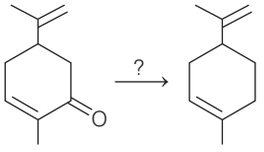
$CH_3CH_2C\equiv N \xrightarrow[\Delta]{(i)\,H_3O^+} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH$
Ethyl cyanide — Propanoic acid

$\xrightarrow{(ii)\,SOCl_2} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-Cl$
Propanoyl chloride

Rosenmund's reaction: $\xrightarrow{(iii)\,Pd/BaSO_4,\,H_2} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H$
Propanaldehyde

Final product of reaction is propanaldehyde.

99



Which of the following reagent is suitable for the preparation of the product in the above reaction?

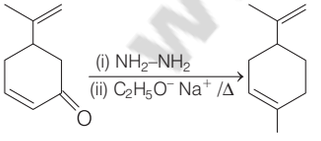
[2021, 24 Feb Shift-II]

(a) $NaBH_4$ (b) $NH_2-NH_2/C_2H_5\overset{\ominus}{O}\overset{\oplus}{Na}$
(c) Ni/H_2 (d) Red P + Cl_2

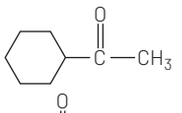
Ans. ***(b)***

To reduce the carbonyl groups into alkane, wolff-Kishner reduction is used, without affecting the double bond.

Wolff-Kishner reagent It utilises hydrazine (NH_2-NH_2) as the reducing agent in the presence of strong base KOH or $C_2H_5\bar{O}Na^+$ in a high boiling protic solvent. The driving force for the reaction is the conversion of hydrazine to nitrogen gas.



100 Which one of the following carbonyl compounds cannot be prepared by addition of water on an alkyne in the presence of $HgSO_4$ and H_2SO_4? **[2021, 24 Feb Shift-II]**

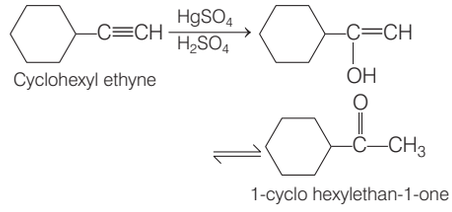
(a) $CH_3-\underset{\underset{O}{\|}}{C}-H$ (b) 

(c) $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H$ (d) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

Ans. ***(c)***

Reaction of $HgSO_4$/dil. H_2SO_4 with alkyne result in addition of water as per Markownikoff's rule.

(a) $HC\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} CH_2=CH-OH \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-H$
Acetylene — Acetaldehyde

(b) 

(c) $CH_3-C\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} CH_3-\underset{OH}{C}=CH_2 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3$
Prop-1-yne — Acetone

Hence $CH_3-CO-CH_3$ cannot be form.

(d) $CH_3C\equiv C-CH_3 \xrightarrow[H_2SO_4]{HgSO_4} CH_3-\underset{OH}{C}=CH-CH_3 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$
But-2-yne — But-2-one

101 Match List-I with List-II.

	List-I	List-II
A.	$R-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow R-CHO$	1. Br_2 /NaOH
B.	$R-CH_2-COOH \longrightarrow R-\underset{Cl}{CH}-COOH$	2. H_2 /Pd - $BaSO_4$
C.	$R-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow R-NH_2$	3. Zn(Hg) / Conc.HCl
D.	$R-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow R-CH_2-CH_3$	4. Cl_2 / Red P, H_2O

Choose the correct answer from the options given below. **[2021, 24 Feb Shift-II]**

	A	B	C	D
(a)	2	1	4	3
(b)	3	4	1	2
(c)	2	4	1	3
(d)	3	1	4	2

Ans. ***(c)***

(A) Alkyl chloride reacts with H_2/Pd-$BaSO_4$ and reduced to alkyl aldehyde. This is known as Rosenmund reduction.

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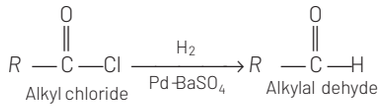
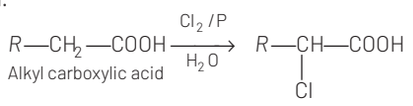


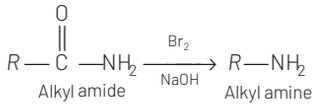
(Rosenmund reduction)

(B) Carboxylic acid reacts with Cl_2 /P in aqueous medium to form 2-chlorocarboxylic acid. This reaction is known as HVZ reaction.



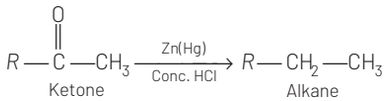
[Hell-Volhard-Zelinsky (HVZ) reaction]

(C) Alkyl amide reacts with Br_2 in presence of NaOH to give alkyl amine. This reaction is known as Hofmann bromide reaction,



(Hofmann bromide reaction)

(D) Ketone reacts with Zn-Hg in presence of conc.HCl to give alkane. This reaction is known as clemmensen reduction.



(Clemmenson reduction)

Hence, correct match is (A)-2, (B)-4, (C)-1, (D)-3.

102 Which of the following reagent is used for the following reaction ?

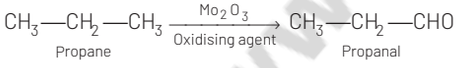
$$CH_3CH_2CH_3 \xrightarrow{?} CH_3CH_2CHO$$

[2021, 24 Feb Shift-I]

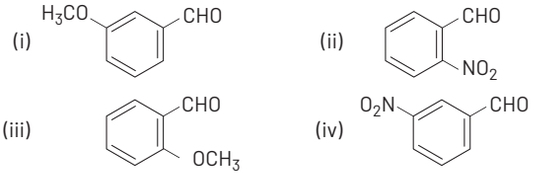
(a) Copper at high temperature and pressure
(b) Molybdenum oxide
(c) Manganese acetate
(d) Potassium permanganate

Ans. ***(b)***

Molybdenum oxide (Mo_2O_3) is used for oxidising alkanes to aldehyde. It used to manufacture molybdenum metal, which serves as an additive to steel and corrosive resistant alloys.



103 The increasing order of the following compounds towards HCN addition is **[2020, 2 Sep Shift-I]**



(a) (i) < (iii) < (iv) < (ii)
(b) (iii) < (iv) < (i) < (ii)
(c) (iii) < (iv) < (ii) < (i)
(d) (iii) < (i) < (iv) < (ii)

Ans. ***(d)***

Addition of HCN to $>C=O$ group of a carbonyl compound follows nucleophilic addition mechanism.

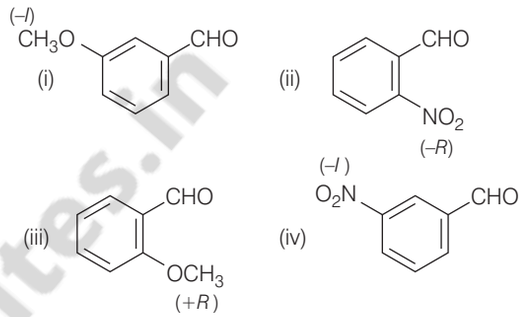
Rate of nucleophilic addition $\propto$ Polarity of the $>\overset{\delta+}{C}=\overset{\delta-}{O}$ group $\propto$ Attachment of electron withdrawing group (EWG), i.e., $-R$ and $-I$ groups, where $-R > -I$

$$\propto \frac{1}{\text{Attachment of electron donating group (EDG)}}$$

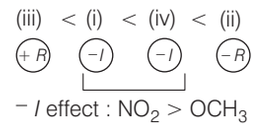
i.e., $+R$ and $+I$ groups

In substituted benzaldehyde, $—NO_2$ (EWG) shows $-R$ effect from *ortho*-and *para*-positions and $-I$ effect (only) from *meta*-positions. The group $—OCH_3$ (EDG) shows $+R$ effect from *ortho*-and *para*-position but $-I$ effect from *meta*-positions.

EWG ($-R > -I$) increases '$\delta+$' character of sp^2 carbon of the $>C=O$ group and hence attack of the nucleophile (CN^-) will be easier.



So, the increasing order of HCN addition is :



$-I$ effect : $NO_2 > OCH_3$

104 The increasing order of the reactivity of the following compounds in nucleophilic addition reaction is :

Propanal, Benzaldehyde, Propanone, Butanone

[2020, 3 Sep Shift-II]

(a) Benzaldehyde < Butanone < Propanone < Propanal
(b) Butanone < Propanone < Benzaldehyde < Propanal
(c) Propanal < Propanone < Butanone < Benzaldehyde
(d) Benzaldehyde < Propanal < Propanone < Butanone

Ans. ***(b)***

Reactivity order toward nucleophilic addition reaction is aldehydes > ketones. Due to the following reasons aldehydes are more reactive than ketones.

(i) Inductive effect An alkyl group has electron donating ($+I$) inductive effect. Hence, greater the number of alkyle group attached to carbonyl group, greater the electron density on carbonyl carbon. Thus, it lowers the attack of nucleophile and hence, reactivity decreases.

(ii) Steric effect Increase in the number of alkyl group attached to carbon results in the attack of nucleophile on carbonyl group becomes more and more difficult due to steric hinderance. Therefore, due to two bulky R groups, ketones are less reactive than aldehydes.

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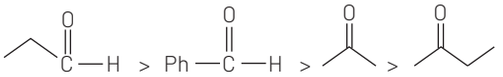
So, the correct reactivity order is



105 The compound, *A* in the following :

$$A \xrightarrow[(ii)\,Conc.\ H_2SO_4/\Delta]{(i)\,CH_3MgBr/H_2O} B \xrightarrow[(ii)\,Zn/H_2O]{(i)\,O_3} C + D$$

$$C \xrightarrow[(ii)\,\Delta]{(i)\,Conc.\ KOH} C_6H_5COO^{\ominus}K^{+} + C_6H_5CH_2OH$$

$$D \xrightarrow[\Delta]{Ba(OH)_2} H_3C{-}\underset{CH_3}{\overset{|}{C}}{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

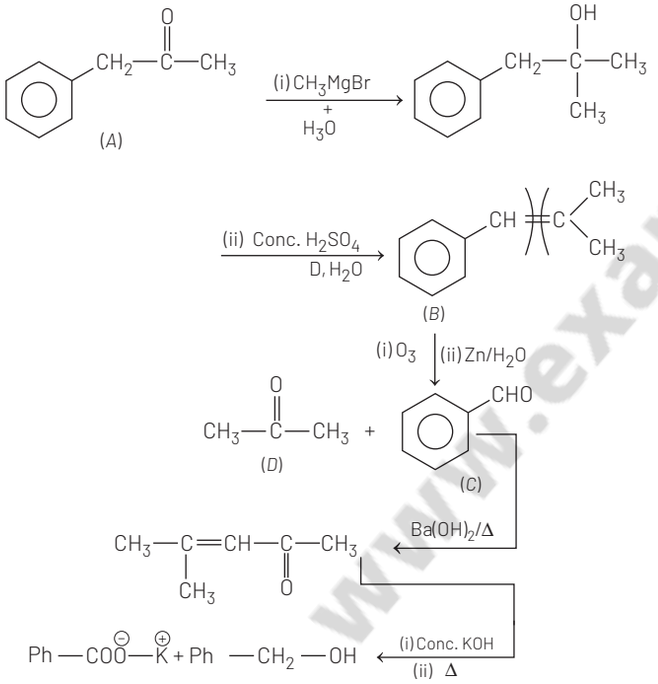
[2020, 3 Sep Shift-II]

(a) $C_6H_5{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$ (b) $C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

(c) $C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_3$ (d) $C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH(CH_3)_2$

Ans. ***(a)***

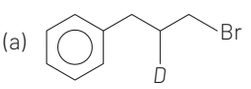
Complete reaction is as follows :

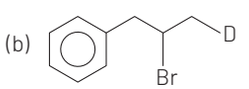


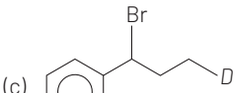
106 The major product [*C*] of the following reaction sequence will be

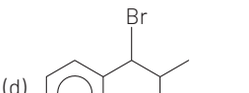
$$CH_2{=}CH{-}CHO \xrightarrow[(ii)\ SOCl_2]{(i)\,NaBH_4} [A] \xrightarrow[Anhy.\ AlCl_3]{} [B] \xrightarrow{DBr} [C]$$

[2020, 4 Sep Shift-II]

(a) 

(b) 

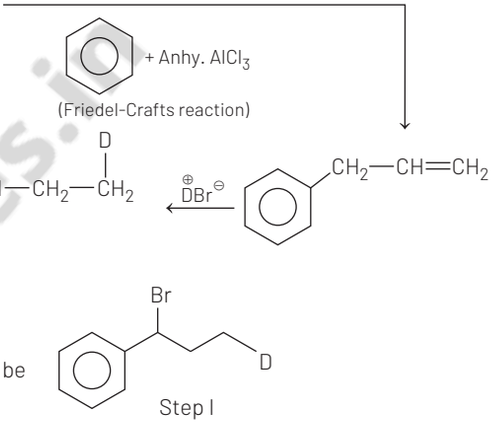
(c) 

(d) 

Ans. ***(c)***

$$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}H \xrightarrow[(ii)\,SOCl_2]{(i)\,NaBH_4} \underset{(A)}{CH_2{=}CH{-}CH_2Cl}$$

(i) $NaBH_4$ reduce $\overset{O}{\overset{\|}{C}}$ group in $-OH$ and then
(ii) $SOCl_2$ react with it



Hence (C) will be

Step I

In the above reaction,

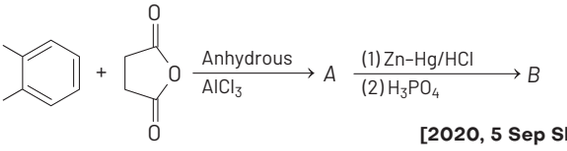
Step I $NaBH_4$ reduce $\overset{O}{\overset{\|}{C}}{-}H$ group into alcohol.

Step II $SOCl_2$ react with this alcohol and form $R\text{-}X$.

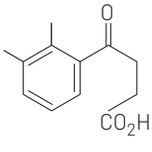
Step III This $R\text{-}X$ react with benzene in the presence of anhydrous $AlCl_3$ *via* Friedel-Crafts reaction and form product.

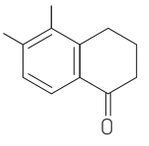
Step IV DBr react with this product and form rearranged product.

107 In the following reaction sequence the major products *A* and *B* are



[2020, 5 Sep Shift-I]

(a) *A* = 

; *B* = 

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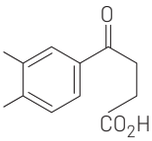
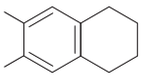
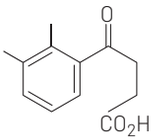
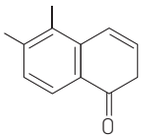
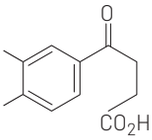
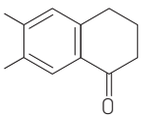
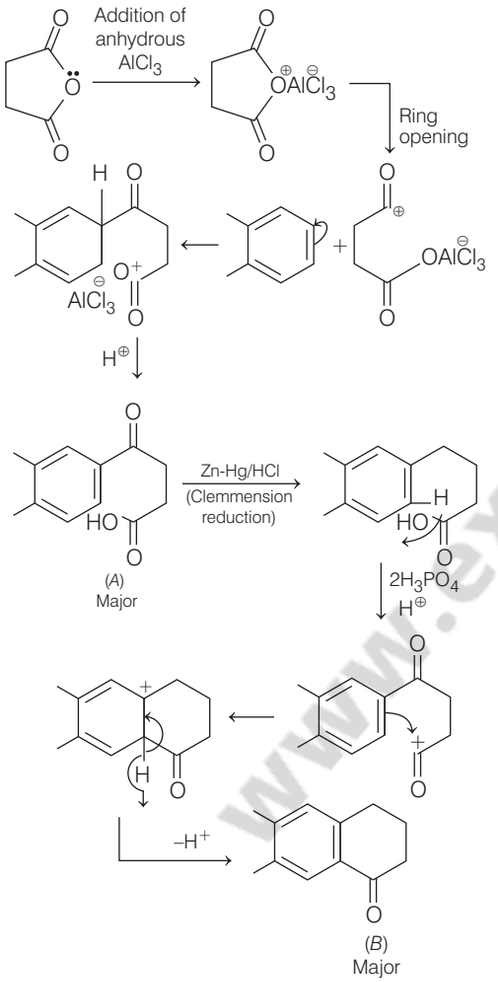
(b) *A* =  ; *B* = 

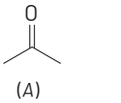
(c) *A* =  ; *B* = 

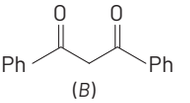
(d) *A* =  ; *B* = 

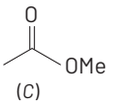
Ans. ***(d)***

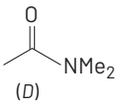


108 The increasing order of the acidity of the α-hydrogen of the following compounds is **[2020, 5 Sep Shift-I]**


(*A*)

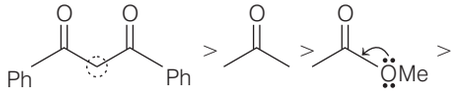

(*B*)


(*C*)

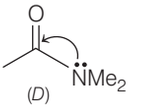

(*D*)

(a) (*D*) < (*C*) < (*A*) < (*B*) (b) (*C*) < (*A*) < (*B*) < (*D*)
(c) (*A*) < (*C*) < (*D*) < (*B*) (d) (*B*) < (*C*) < (*A*) < (*D*)

Ans. ***(a)***


(*B*) (*A*) (*C*)

Active methylene (highly acidic) (In this case most stable anion is formed)


(*D*)

Lower-M (mesomeric) effect as compaired to —C(=O)— group

Compound (*B*) is a active methylene compound is highly resonance stabilised. This compound possessing a methylene bridge located between two strong electron withdrawing groups (such as carbonyl group). So, it is highly acidic in nature.

Compounds (*C*) and (*D*) having electron donating group. Which decreases the acidity and compound (*A*) is more acidic than (*C*) and (*D*) because it does not contain any electron releasing group.

Hence option (a) is correct.

(*D*) < (*C*) < (*A*) < (*B*)

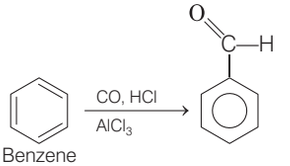
109 The correct match between Item-I (starting material) and Item-II (reagent) for the preparation of benzaldehyde is **[2020, 6 Sep Shift-II]**

	Item - I		Item - II
I	Benzene	(P)	HCl and $SnCl_2$, H_3O^+
II	Benzonitrile	(Q)	H_2, Pd-$BaSO_4$, S and quinoline
III	Benzoyl chloride	(R)	CO, HCl and $AlCl_3$

(a) (I) - (Q), (II) - (R) and (III) - (P) (b) (I) - (P), (II) - (Q) and (III) - (R)
(c) (I) - (R), (II) - (P) and (III) - (Q) (d) (I) - (R), (II) - (Q) and (III) - (P)

Ans. ***(c)***

(I) Given, reaction is Gattermann -Koch reaction involves the formation of an aryl aldehyde using CO and HCl as reactants. The reaction catalysed by $AlCl_3$.



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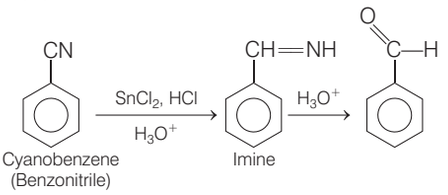
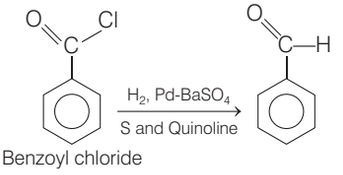
(II) Given, reaction is Stephen reduction reaction involves the preparation of aldehydes from nitriles using tin (II) chloride, hydrochloric acid and quenching the resulting minimum salt with water.



(III) Given, reaction is Rosenmund reduction is a hydrogenation process in which an acyl chloride is selectively reduced to an aldehyde.



Correct match of Item-I and Item-II will be

(I) - (R), (II) - (P) and (III) - (Q).

110 Consider the following reactions :

$(A)(CH_3)_3CCH(OH)CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$

$(B)(CH_3)_2CHCH(Br)CH_3 \xrightarrow{\text{Alc. KOH}}$

$(C)(CH_3)_2CHCH(Br)CH_3 \xrightarrow{(CH_3)_3O^{\ominus}K^{\oplus}}$

$(D)(CH_3)_2\underset{\underset{OH}{|}}{C}—CH_2—CHO \xrightarrow{\Delta}$

Which of these reaction(s) will not produce Saytzeff product? **[2020, 7 Jan Shift-I]**

(a) (A), (C) and (D) (b) (B) and (D)

(c) Only (C) (d) Only (D)

Ans. ***(c)***

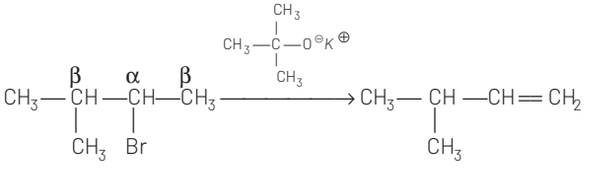
In a β-elimination reaction, a leaving group (like Cl^-) leaves along with a hydrogen (as H^+) from a β-position. Among available β-positions, H^+ removal is preferred to take place from the β-position having least H atoms according to Saytzeff's rule.

But in reaction (c),

the major product is not Saytzeff 's product

because the given base, $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—O^-$ is bulky and ∴ due to steric hinderance removes H^+ from $—CH_3$ group.

In this case reaction occurs as :



The major product is called Hofmann product.

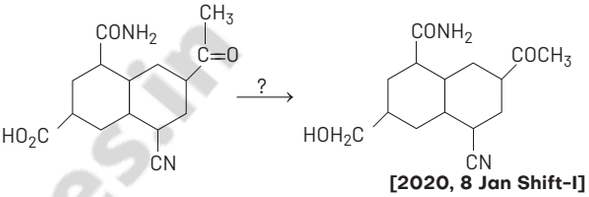
The rest of the given reactions produce Saytzeff products as follows :

(a) $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow{\text{Conc. } H_2SO_4} CH_3—\underset{\underset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}—CH_3$

(b) $CH_3—\overset{\beta}{\underset{\underset{CH_3}{|}}{CH}}—\overset{\alpha}{\underset{\underset{Br}{|}}{CH}}—\overset{\beta}{CH_3} \xrightarrow{\text{Alc. KOH}} CH_3—\underset{\underset{CH_3}{|}}{C}=CH—CH_3$

(d) $\overset{\beta}{\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{CH_3—\overset{\alpha}{C}—CH_2}}}—CHO \xrightarrow{\Delta} CH_3—\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}=\underset{\underset{CHO}{|}}{C}—H$

111 The most suitable reagent for the given conversion is

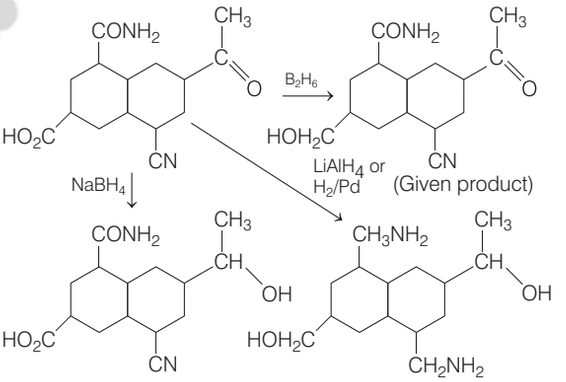


[2020, 8 Jan Shift-I]

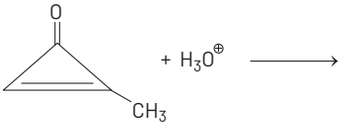
(a) B_2H_6 (b) $LiAlH_4$ (c) $NaBH_4$ (d) H_2 / Pd

Ans. ***(a)***

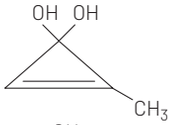
The most suitable reagent for the given conversion is B_2H_6.

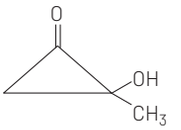


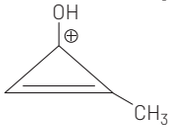
112 The major product in the following reaction is

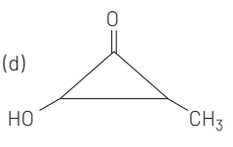


[2020, 8 Jan Shift-II]

(a) 

(b) 

(c) 

(d) 

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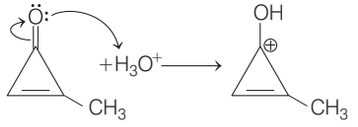
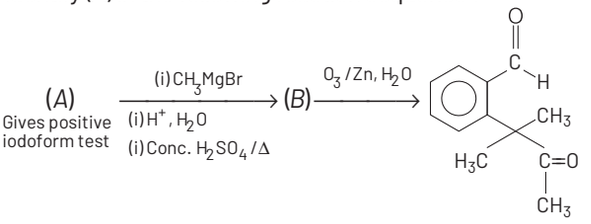
Ans. ***(c)***

Option (c) is the major product formed.

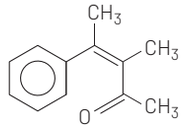


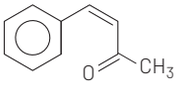
Aromatic product

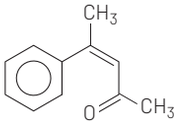
113 Identify (*A*) in the following reaction sequence :

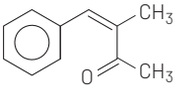


[2020, 9 Jan Shift-I]

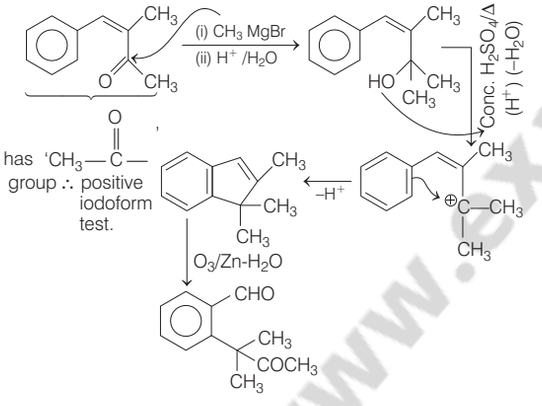
(a) 

(b) 

(c) 

(d) 

Ans. ***(d)***



114 Consider the following reactions :

$$A \xrightarrow[(ii)\,H_3O^+]{(i)\,CH_3MgBr} B \xrightarrow[573\ K]{Cu} \text{2-methyl- 2- butene}$$

The mass percentage of carbon in *A* is .....

[2020, 9 Jan Shift-II]

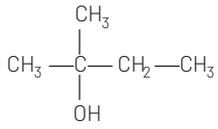
Ans. ***(66.67)***

On reversing the given reaction we can get the *A* and *B*.

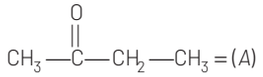
$$B \xrightarrow[573\ K]{Cu} CH_3-\underset{\text{2 methyl-2 -butene}}{\overset{CH_3}{\overset{|}{C}}}=CH-CH_3$$

∴ *B* must be a 3° alcohol that, on oxidation produces alkene.

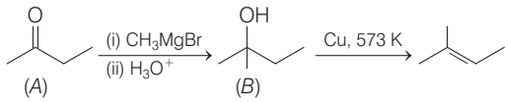
So, the structure of *B* is



To get *B* (alcohol) CH_3MgBr must react with a ketone.



Complete reaction is as follows :

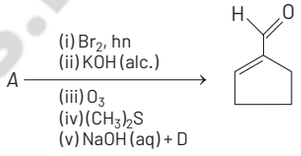


% C by mass

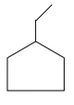
$$= \frac{\text{mass of C } (= 4\times 12)\times 100}{\text{total molar mass } [= 4\times 12 + (16) + (8\times 1)]}$$

$$= \frac{48\times 100}{72} = 66.67\%$$

115 In the following reaction *A* is **[2020, 9 Jan Shift-II]**



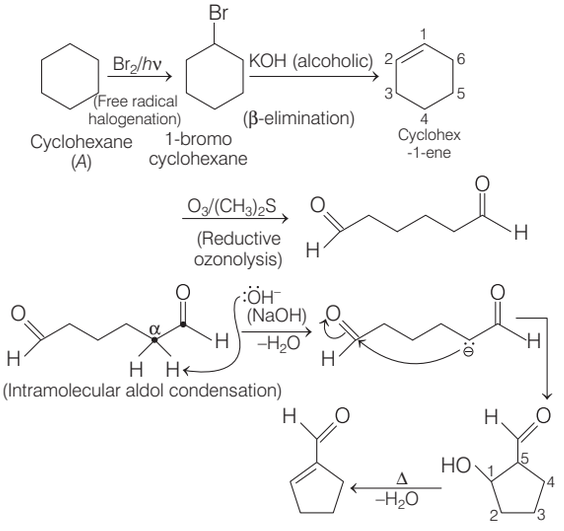
(a)

(b) 

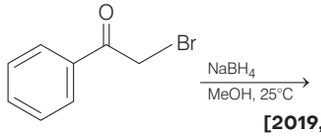
(c)

(d)

Ans. ***(c)***



116 The major product of the following reaction is



[2019, 8 April Shift-I]

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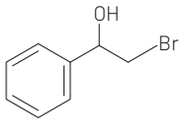
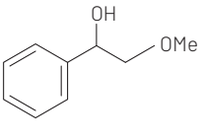
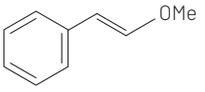
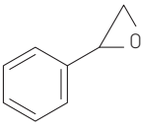
(a) 

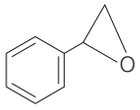
(b) 

(c) 

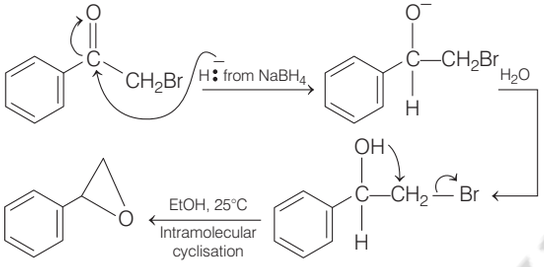
(d) 

Ans. ***(d)***

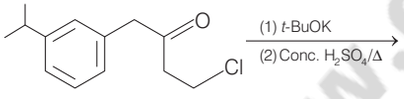
Major product obtained in the given reaction is



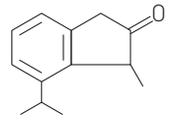
$NaBH_4$ in the reaction is used for the reduction by addition of a hydride ion and a proton. Carbon-oxygen double bonds are easily reduced by sodium borohydride. The actual reducing agent in these reductions is hydride ion (H^-). Hydride ion adds to the carbonyl carbon and the alkoxide ion that is formed is subsequently protonated by water. In other words, the carbonyl group is reduced by adding an H^- followed by an H^+. The mechanism of the given reaction is as follows :

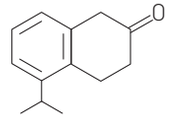


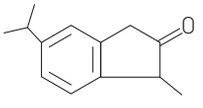
117 The major product of the following reaction is

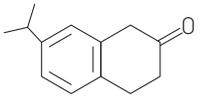


[2019, 8 April, Shift-II]

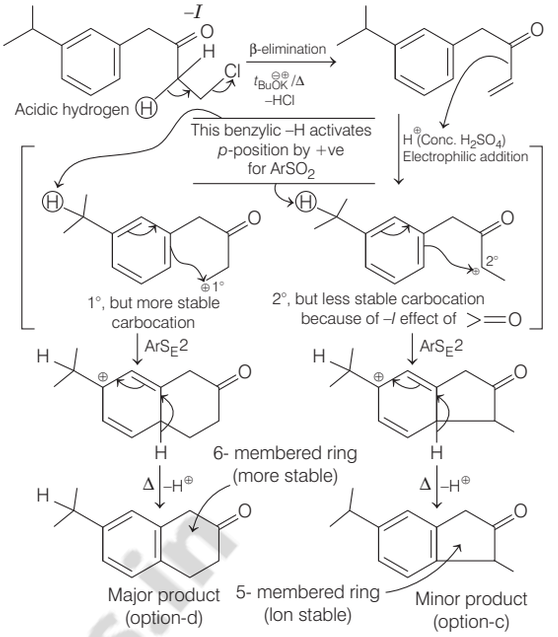
(a) 

(b) 

(c) 

(d) 

Ans. ***(d)***



118 In the following reaction,

Carbonyl compound + MeOH $\overset{HCl}{\rightleftharpoons}$ acetal Rate of the reaction is the highest for:

(a) Acetone as substrate and methanol in excess
(b) Propanal as substrate and methanol in stoichiometric amount
(c) Acetone as substrate and methanol in stoichiometric amount
(d) Propanal as substrate and methanol in excess

[2019, 9 April Shift-II]

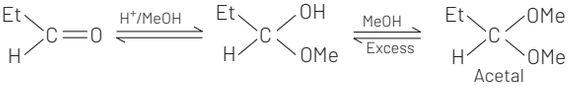
Ans. ***(d)***

Key Idea Aldehydes are more reactive than ketones in nucleophilic addition reactions.

For the reaction,

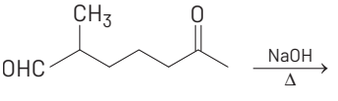
Carbonyl compound + MeOH $\overset{HCl}{\rightleftharpoons}$ Acetal

Rate of reaction is the highest for propanal as substrate and methanol in excess. Propanal is an aldehyde and more reactive than ketones. When MeOH is taken in excess then reaction moves in the forward direction that results in the formation of acetal. Reaction involved is as follows :



119 The major product obtained in the following reaction is

[2019, 8 April Shift-II]



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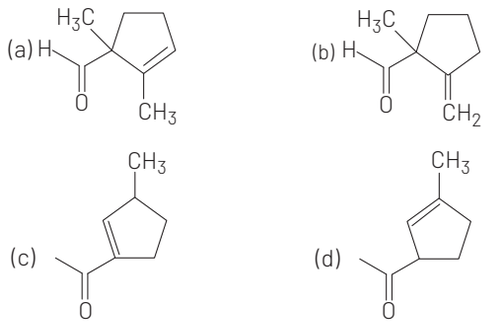
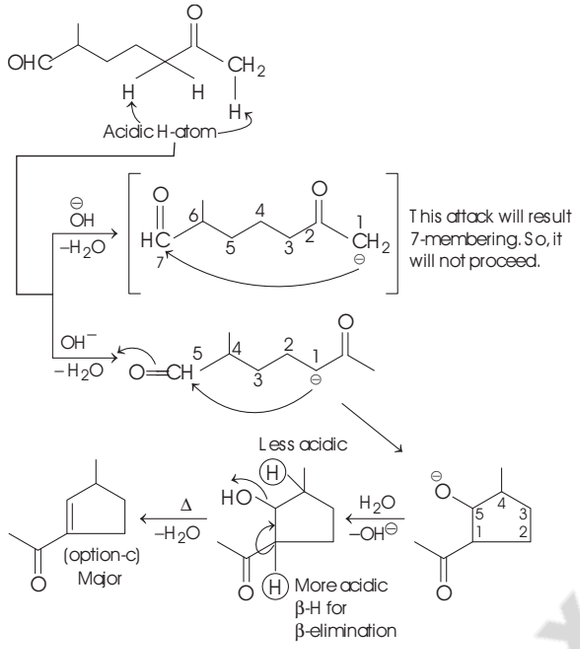
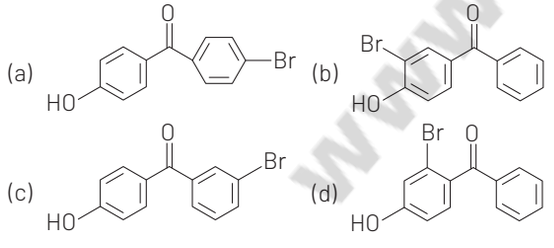


Ans. ***(c)***

It is in intermolecular aldol condensation reaction.

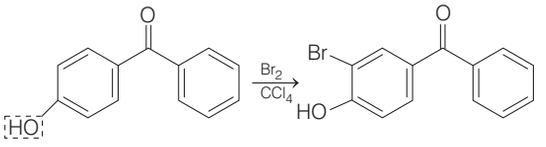


120 *p*-hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives **[2019, 9 April Shift-II]**



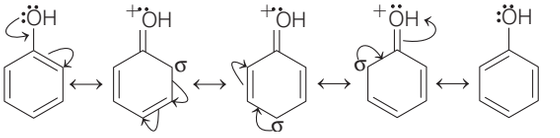
Ans. ***(b)***

p-hydroxy benzophenone upon reaction with bromine in carbon tetrachloride gives 3-bromo-4-hydroxy benzophenone.

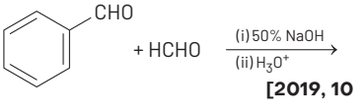


—OH group attached on the benzene ring direct the incoming group at *ortho* and *para*-positions due to increase in electron density at *o* and *p*-positions. —OH group also exhibit –I group that reduces the electron density to some extent at *o* and *p*-positions. But overall electron density increases at these positions of the ring due to resonance. Hence, attack of —Br occur at *ortho-position.*

Resonating structures are as follows:

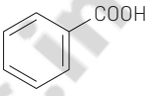


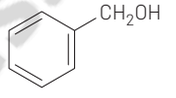
121 Major products of the following reaction are

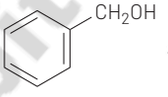
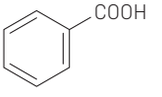


[2019, 10 April Shift-I]

(a) CH_3OH and HCO_2H

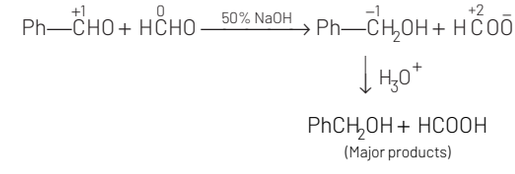
(b) CH_3OH and 

(c) HCOOH and 

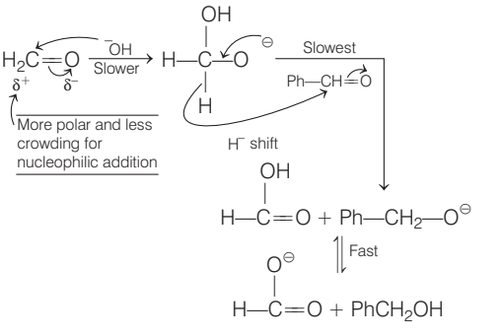
(d)  and 

Ans. ***(c)***

The given reaction is a crossed Cannizzaro reaction which is a redox reaction too. Oxidation number of carbon atom of the —CHO groups of Ph—CHO and H—CHO are +1 and zero respectively. So, HCHO is the stronger reducing agent than PhCHO. As a result, HCHO is oxidised to HCOONa (by donation of hydride, H^-) and PhCHO (H^- acceptor) is reduced to $PhCH_2OH$.



The reaction proceed *via* following mechanism.



Thus, the correct option is (c).

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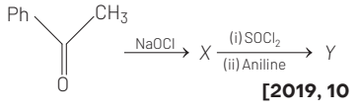
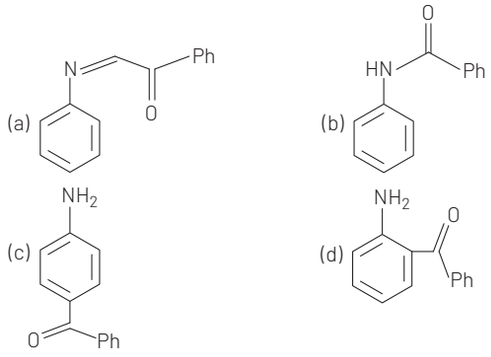
122 The major product *Y* in the following reaction is



[2019, 10 April Shift-II]

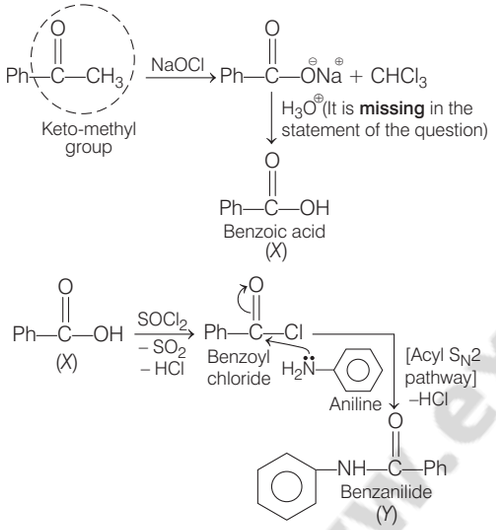


Ans. ***(b)***

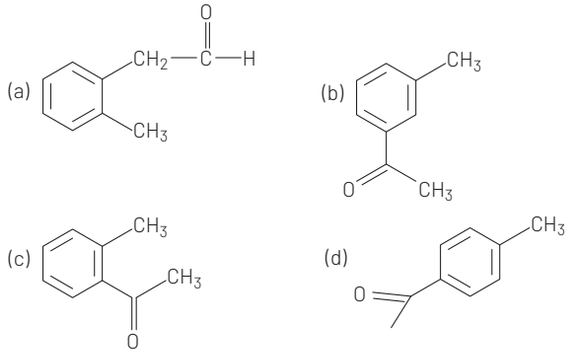
NaOCl (sodium hypochlorite) is the reagent of haloform (chloroform formation) reaction.

$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

The given reaction takes place as follows :



123 Compound *A* ($C_9H_{10}O$) shows positive iodoform test. Oxidation of *A* with $KMnO_4$ / KOH gives acid *B* ($C_8H_6O_4$). Anhydride of *B* is used for the preparation of phenolphthalein. Compound *A* is **[2019, 10 April Shift-II]**



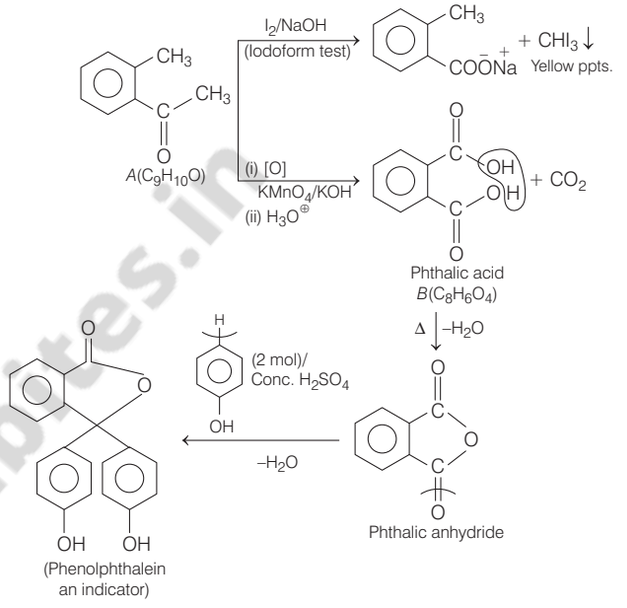
Ans. ***(c)***

(i) $C_9H_{10}O$ shows positive iodoform test thus, $-\overset{\overset{O}{\|}}{C}-CH_3$ group is present.

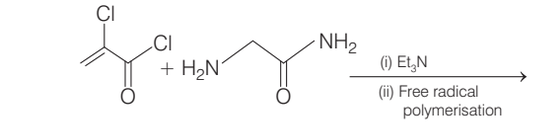
(ii) $C_9H_{10}O$ on strong oxidation ($KMnO_4$ /KOH), gives acid ($C_8H_6O_4$), indicating it can be a dicarboxylic acid. So, 'A' contains $-COCH_3$ and one $-CH_3$ group which get oxidised into $-COOH$ and $-COOH$ respectively.

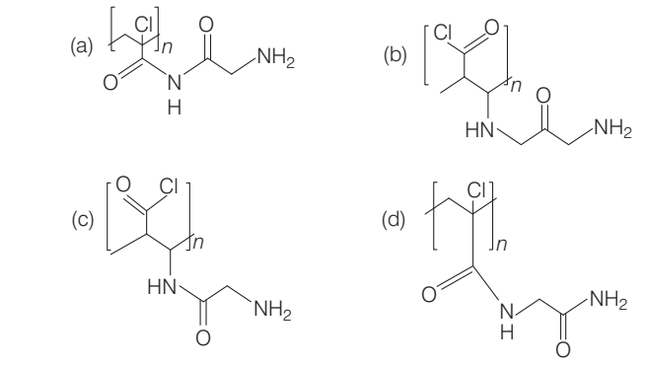
(iii) In the preparation of phenolphthalein from phenol, phthalic anhydride is used. So, '*B*' can be phthalic acid (benzene-1,2-dicarboxylic acid) which readily forms anhydride.

Thus, the reaction sequence is as follows :



124 Major product of the following reaction is





[2019, 9 Jan Shift-I]

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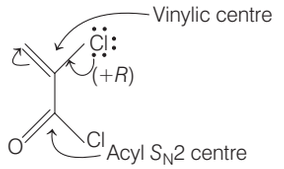
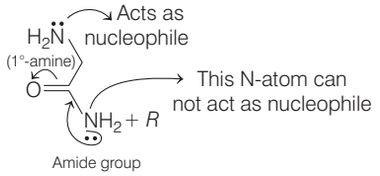
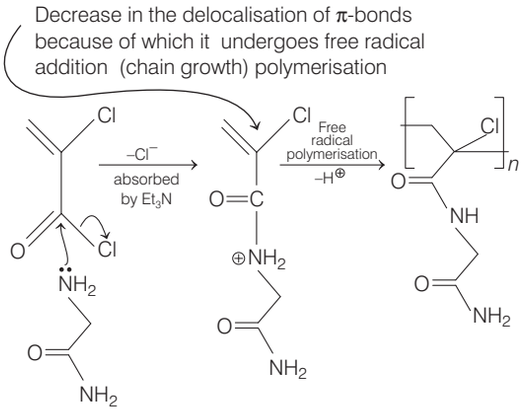
Ans. ***(d)***

The analysis of both the substrates :

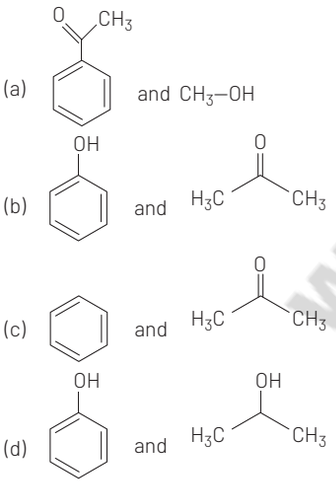




So, the reaction can take place as follows :



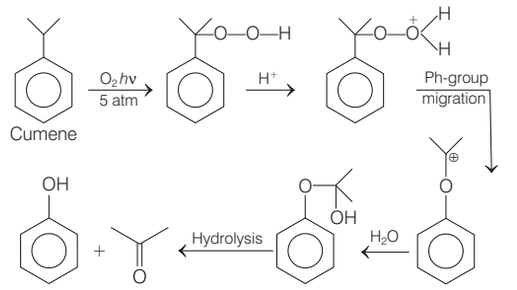
125 The products formed in the reaction of cumene with O_2 followed by treatment with dil. HCl are



[2019, 9 Jan Shift-I]

Ans. ***(b)***

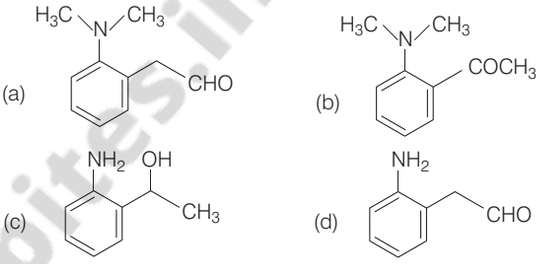
The given process is cumene process (Hock process) to synthesise phenol and acetone industrially. In Hock p rocess, Ph– group migrate and release H_2O.



126 The tests performed on compound *X* and their inferences are :

	Test	Inference
(a)	2, 4- DNP test	Coloured precipitate
(b)	Iodoform test	Yellow precipitate
(c)	Azo-dye test	No dye formation

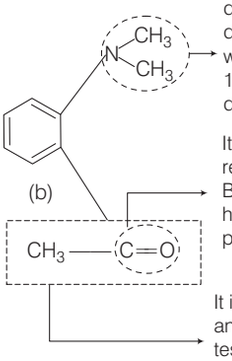
Compound '*X*' is



[2019, 9 Jan Shift-II]

Ans. ***(b)***

Let us study the chemical nature of the functional groups present in the following compound (b).



It is a 3°-amino group (—NMe_2) though aromatic which will not respond to diazotisation ($NaNO_2$ + dil. HCl/5°C). So, formation of diazonium ion and its further reaction with alkaline phenol or β-napthol at 5-10°C to produce a precipitate of azo-dye will not take place.

It is a keto group $>C=O$ and so it responds to 2, 4-DNP test with Brady's reagent (2, 4-dinitrophenyl hydrazine) to give a reddish orange precipitate.

It is a keto-methyl group $-\overset{O}{\overset{\|}{C}}-CH_3$ and hence, it responds to iodoform test to give a yellow precipitate of iodoform (CHI_3).

Compound (c) is an alcohol and does not give positive 2,4-DNP test. Hence, eliminated.

(a) and (d) does not have $-CH_3CO$ group and does not give iodoform test. Hence, eliminated.

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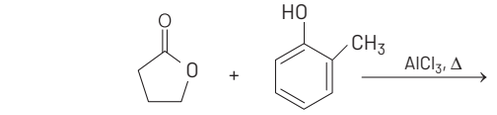
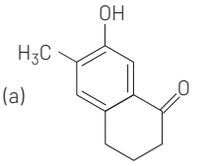
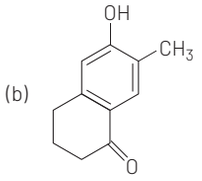
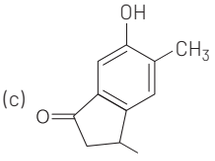
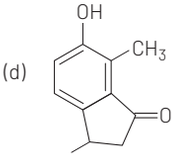
127 The major product of the following reaction is



(a) 

(b) 

(c) 

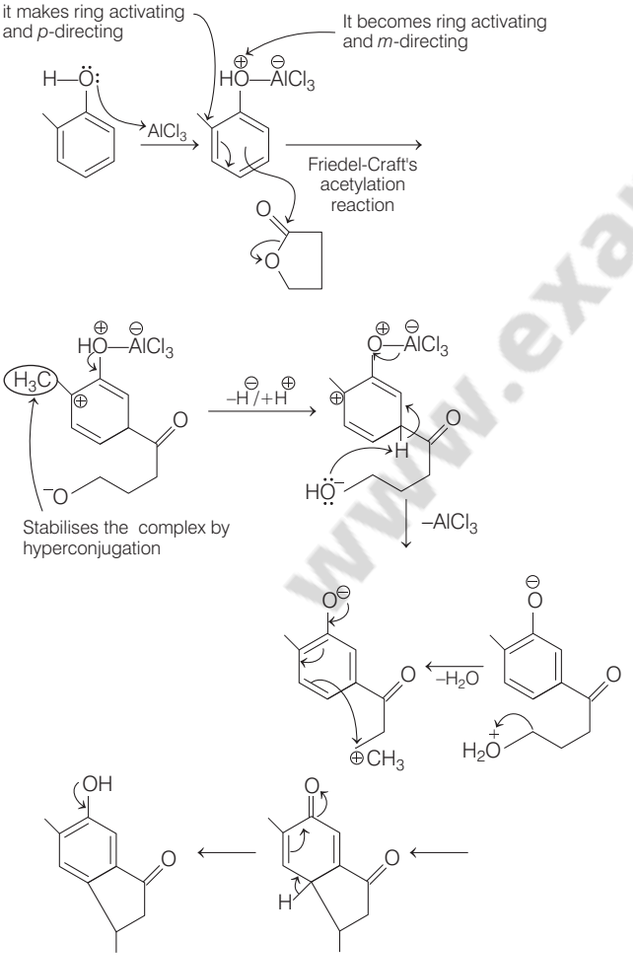
(d) 

[2019, 9 Jan Shift-II]

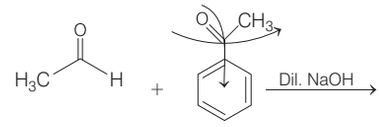
Ans. ***(c)***

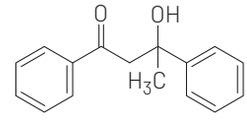
It is an aromatic electrophilic substitution reaction (Ar S_E2).

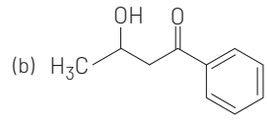
The reaction follows Ar S_E2 (Aromatic electrophlic substitution pathway) as shown below :

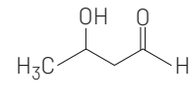


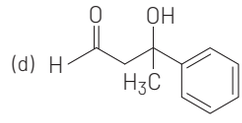
128 The major product formed in the following reaction is



(a) 

(b) 

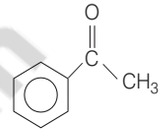
(c) 

(d) 

[2019, 9 Jan Shift-II]

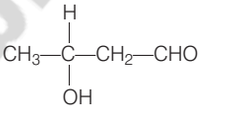
Ans. ***(c)***

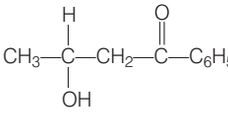
In aldol condensation, generally aldehydes react at a faster rate than ketones towards base. In the given case CH_3CHO will lose

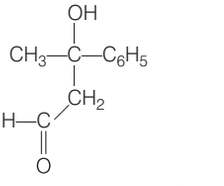
α-hydrogen faster than 

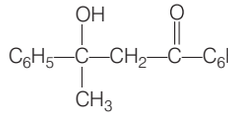
to one more reason, i.e. conjugation between benzene ring and $>C=O$ group. Along with sterically less hindered nucleophile of CH_3CHO will also add to the major product formation.

Following four products are possible in the reaction:

(i)  (Self Aldol condensation of CH_3CHO)

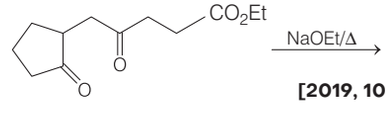
(ii)  (Cross Aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which $>C=O$ group of CH_3CHO is carbanion acceptor).

(iii)  (Cross Aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which $>C=O$ group of $C_6H_5COCH_3$ is carbanion acceptor).

(iv)  (Self Aldol condensation product of $C_6H_5COCH_3$)

$\bar{O}H$ of base will prefer to attack on $—CH_3$ group of CH_3CHO for the formation of carbanion and as among the $>C=O$ groups available, the $>C=O$ group of CH_3CHO is the best carbanion acceptor. Hence, self condensation product of CH_3CHO will be the major product.

129 The major product obtained in the following reaction is



[2019, 10 Jan Shift-II]

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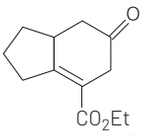
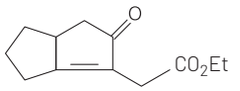
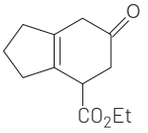
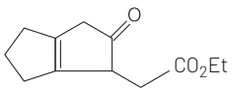
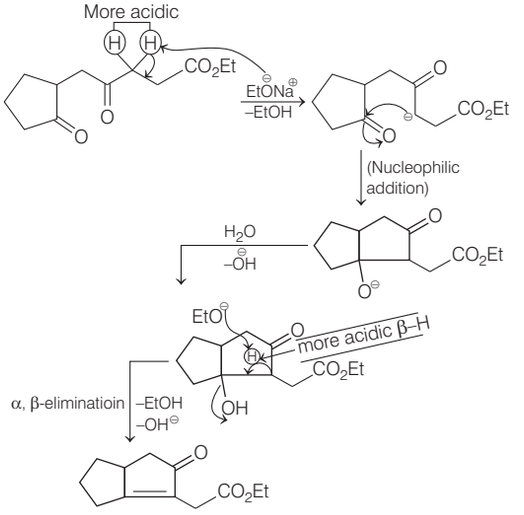
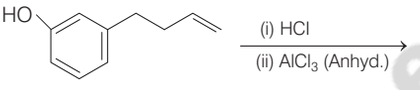
(a) 
(b) 
(c) 
(d) 

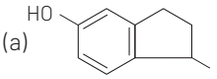
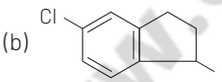
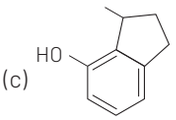
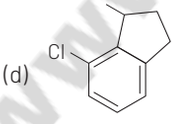
Ans. ***(b)***

In presence of strong base, acidic H can easily be removed that result in formation of anion. The resulting anion undergoes intramolecular nucleophilic addition which on hydrolysis followed by heating gives the required product.



130 The major product of the following reaction is

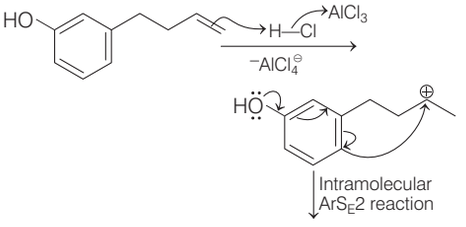


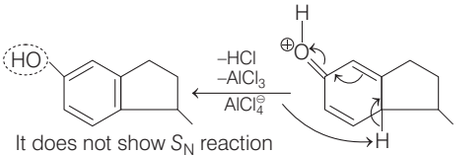
(a) 
(b) 
(c) 
(d) 

[2019, 11 Jan Shift-II]

Ans. ***(a)***

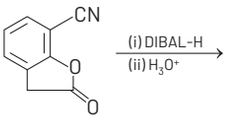
In the given reaction, $AlCl_3$ helps in the generation of electrophile that further undergoes ArS_E2 reaction to give the required product.

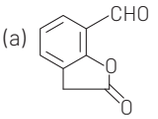
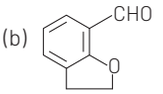
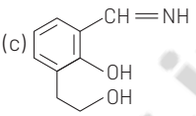
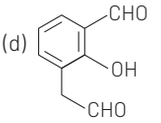




It does not show S_N reaction with HCl because of double bond nature of the O—C bond, (due to +*R*-effect of the —OH group.)

131 The major product of the following reaction is

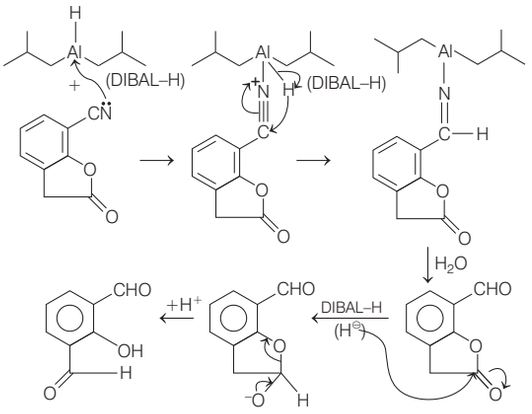


(a) 
(b) 
(c) 
(d) 

[2019, 12 Jan Shift-I]

Ans. ***(d)***

DIBAL-H (Diisobutylaluminium hydride) is a reducing agent with formula [(i-Bu_2AlH]. At ordinary temperatures, nitriles give imines which are readily converted in aldehydes by hydrolysis whereas lactones are reduced directly to aldehydes.



132 In the following reaction,

$$\text{Aldehyde} + \text{Alcohol} \xrightarrow{HCl} \text{Acetal}$$

Aldehyde	Alcohol	Aldehyde	Alcohol
HCHO	^{t}BuOH	CH_3CHO	MeOH

The best combination is **[2019, 12 Jan Shift-I]**

(a) CH_3CHO and MeOH (b) CH_3CHO and ^{t}BuOH
(c) HCHO and MeOH (d) HCHO and ^{t}BuOH

Ans. ***(c)***

Acetal formation is nucleophilic addition reaction due to the addition of alcohols on aldehydes. The reactivity of nucleophilic addition depends on following two factors.

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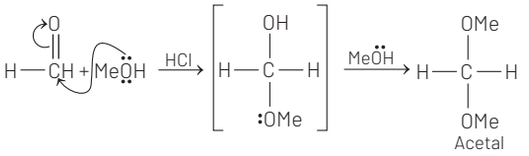
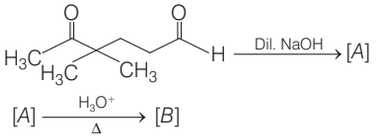
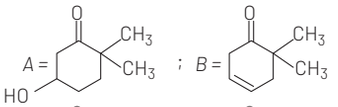
- Inductive effect Greater the number of alkyl group attached to carbonyl group, greater is the electron density on carbonyl carbon. Thus, lowers the attack of nucleophile. Hence, reactivity decreases.
- Steric effect As the number of alkyl group attached to carbonyl carbon increases, the attack of nucleophile on carbonyl group becomes more difficult due to steric hinderance.

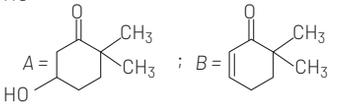
Thus, the best combination is HCHO and MeOH. The reaction is as follows:

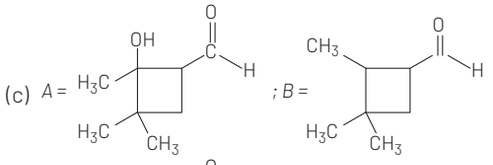


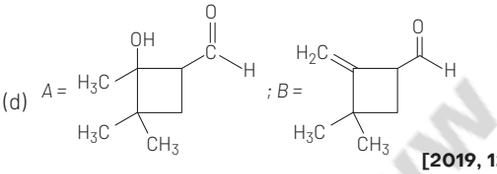
133 In the following reactions, products *A* and *B* are



(a) 

(b) 

(c) 

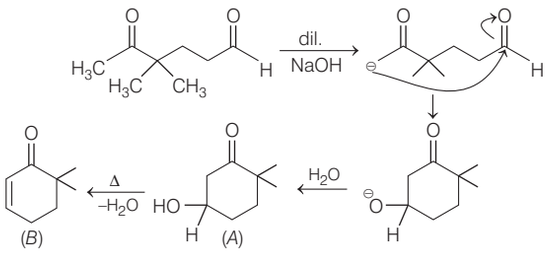
(d) 

[2019, 12 Jan Shift-I]

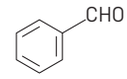
Ans. ***(b)***

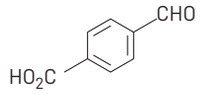
The reactant in presence of Dil. NaOH undergoes intramolecular aldol condensation reaction.

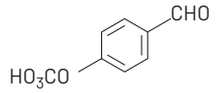
As a result of this, β-hydroxyketone (*A*) is obtained which on hydrolysis followed by heating produces α, β-unsaturated ketone (B)

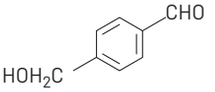


134 The aldehydes which will not form Grignard product with one equivalent Grignard reagents are

(*A*) 

(*B*) 

(*C*) 

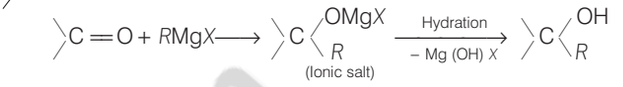
(*D*) 

(a) (*C*), (*D*)
(b) (*B*), (*D*)
(c) (*B*), (*C*), (*D*)
(d) (*B*), (*C*)

[2019, 12 Jan Shift-II]

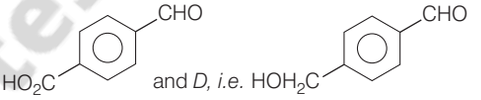
Ans. ***(b)***

Key Idea Grignard reagent usually attacks on > C═O group as $\rangle C^{\delta+}{=}O^{\delta-}$

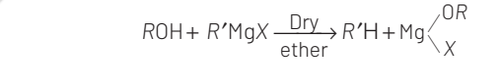


The question is related to above reaction only with the condition that the consumption of *R*Mg*X* will be more than 1 equivalent in some of the given cases.

Among the given compounds *B*, i.e.



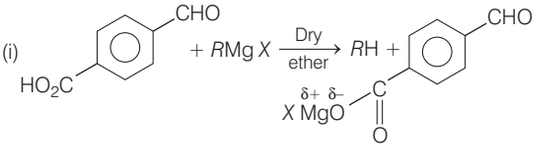
contain additional groups which can give active hydrogens. Grignard reagents produce alkanes whenever come in contact with any group or compound which can give active hydrogen as:

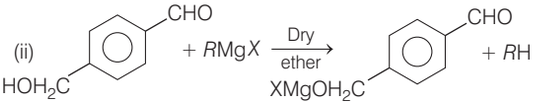


These reactions are equivalent to acid-base reactions. So, in both of these compounds more than one equivalent will be required to form Grignard products. Remember these compounds will give 2 type of products as:

(i) from the > C═O group
(ii) from the group which release active hydrogen

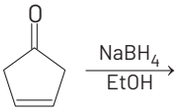
The additional reactions involved are:

(i) 

(ii) 

135 The major product of the following reaction is

[2019, 12 Jan Shift-II]



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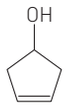
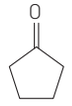
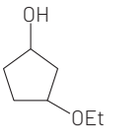
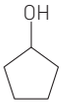
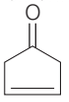
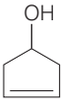
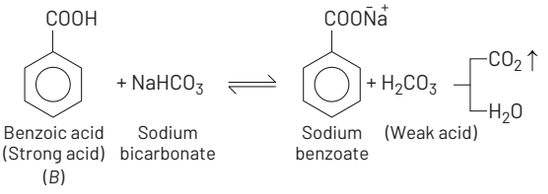
(a)  (b)  (c)  (d) 

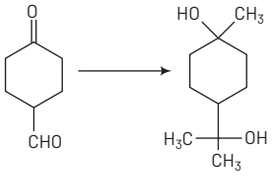
Ans. ***(a)***

Reducing agents like $LiAlH_4$, $NaBH_4$, i.e. complex hydrides usually does not affect olifenic or π-bonds. Thus, if $NaBH_4$ is applied to a compound like  then its $>C=O$ bond will be reduced only and we get  as the final product.

136 The correct sequence of reagents for the following conversion will be **[JEE Main 2017]**

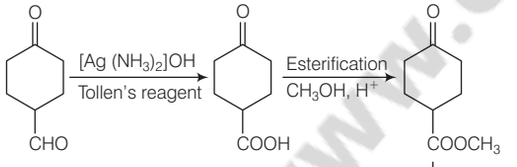


Benzoic acid (Strong acid) (*B*) — Sodium bicarbonate — Sodium benzoate — (Weak acid)

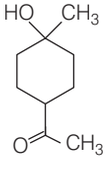


(a) $[Ag(NH_3)_2]^+ OH^-$, H^+ / CH_3OH, CH_3MgBr
(b) CH_3MgBr, H^+ / CH_3OH, $[Ag(NH_3)_2]^+ OH^-$
(c) CH_3MgBr, $[Ag(NH_3)_2]^+ OH^-$, H^+ / CH_3OH
(d) $[Ag(NH_3)_2]^+ OH^-$, CH_3MgBr, H^+ / CH_3OH

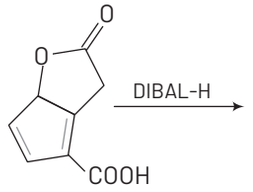
Ans. ***(a)***



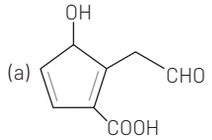
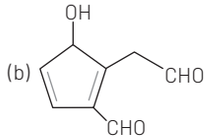
Before final product is formed, intermediate is

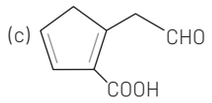
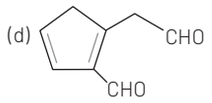


137 The major product obtained in the following reaction is



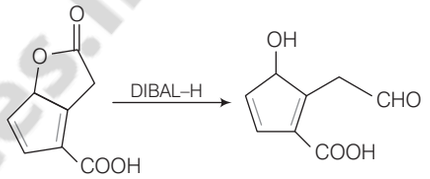
[JEE Main 2017]

(a)  (b) 

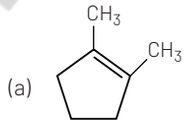
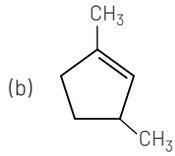
(c)  (d) 

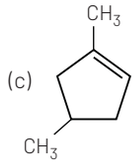
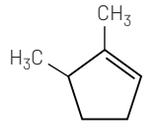
Ans. ***(a)***

DIBAL-H (Di-isobutyl aluminium hydride) is a reducing agent with formula. This is generally used for the preparation of aldehydes. Using DIBAL –H, Lactones are reduced directly to aldehydes.

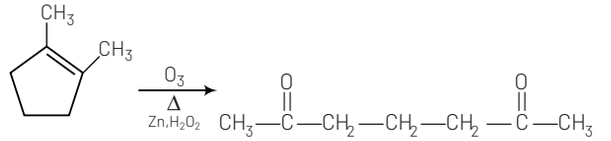


138 Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? **[JEE Main 2015]**

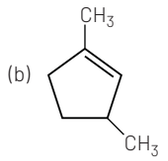
(a)  (b) 

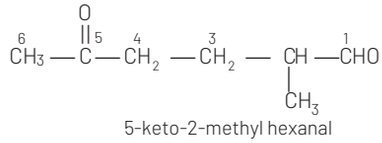
(c)  (d) 

Ans. ***(b)***



Heptan-2,6-dione

(b) 



5-keto-2-methyl hexanal

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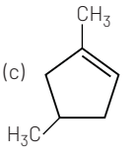
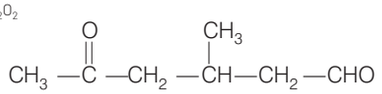
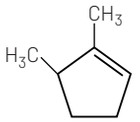
(c) 

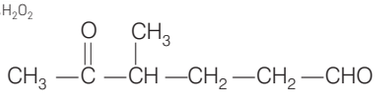
$\xrightarrow[\Delta]{O_3}$ $\xrightarrow[Zn,H_2O_2]{}$



5-keto-3-methyl hexanal

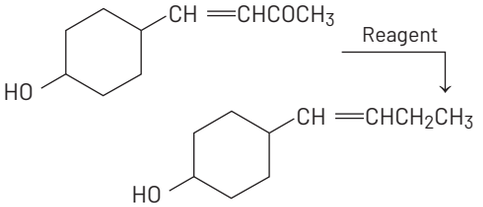
(d) 

$\xrightarrow[\Delta]{O_3}$ $\xrightarrow[Zn,H_2O_2]{}$



5-keto-4-methyl hexanal

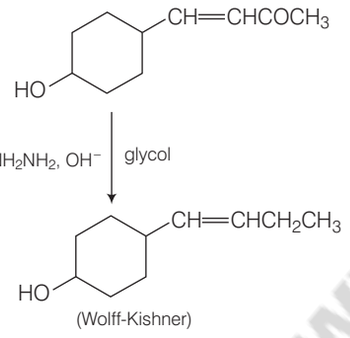
139 In the given transformation, which the following is the most appropriate reagent? **[AIEEE 2012]**



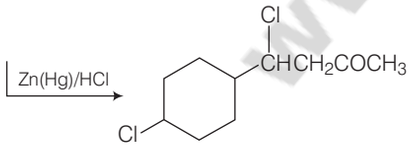
(a) $NH_2NH_2, \overset{\ominus}{O}H$ (b) Zn -Hg / HCl

(c) Na, Liq. NH_3 (d) $NaBH_4$

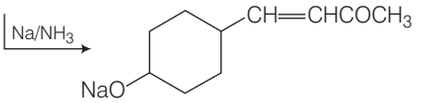
Ans. ***(a)***

(a) 

(Wolff-Kishner)

(b) 

HCl attacks 2° alcohol as well as (C=C) bond.

(c) 

(d) $NaBH_4$ Low yield

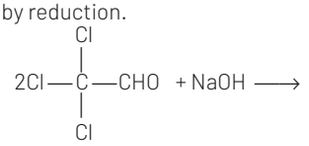
140 Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is **[AIEEE 2011]**

(a) 2, 2, 2-trichlorethanol (b) trichloromethanol

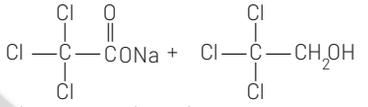
(c) 2, 2, 2-trichloropropanol (d) chloroform

Ans. ***(a)***

Cannizzaro's reaction is given by aldehydes (*R*CHO) lacking H at α-carbon or lacking α-carbon (as in HCHO). With NaOH, there is formation of acid salt ($RCOO^-$) by oxidation and alcohol (RCH_2OH) by reduction.



a-carbon without H



(By oxidation) (By reduction 2, 2, 2, trichloroethanol)

141 Silver mirror test is given by which one of the following compounds? **[AIEEE 2011]**

(a) Acetaldehyde (b) Acetone

(c) Formaldehyde (d) Benzophenone

Ans. ***(a, c)***

All aldehydes including reducing sugar (as glucose, fructose) gives Silver-mirror test (with Tollen's reagent)

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\Delta} RCOO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

Silver mirror (R=H, CH_3)

Thus, acetaldehyde and formaldehyde give silver-mirror test.

142 Ozonolysis of an organic compound *A* produces acetone and propionaldehyde in equimolar mixture. Identify *A* from the following compounds. **[AIEEE 2011]**

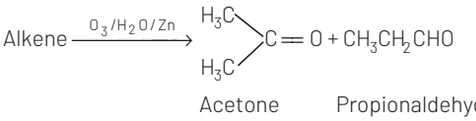
(a) 2-methyl-1-pentene

(b) 1-pentene

(c) 2-pentene

(d) 2-methyl-2-pentene

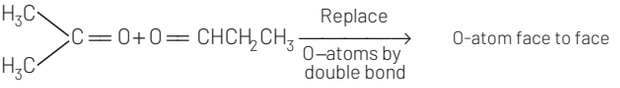
Ans. ***(d)***

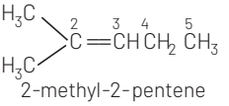


Acetone Propionaldehyde

To identify alkene (from ozonolysis products) place these products with O-atoms face to face.

Replace O-atoms by = (double) bond.





2-methyl-2-pentene

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143 One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is **[AIEEE 2010]**

(a) propene (b) 1-butene (c) 2-butene (d) ethene

Ans. ***(c)***

The general molecular formula for carbonyl compound is $C_nH_{2n}O$.

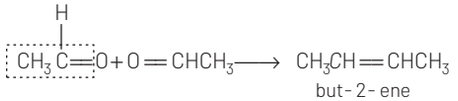
$\Rightarrow$ $C_nH_{2n}O = 44\ u$

$\Rightarrow$ $C_nH_{2n} = 44 - 16$

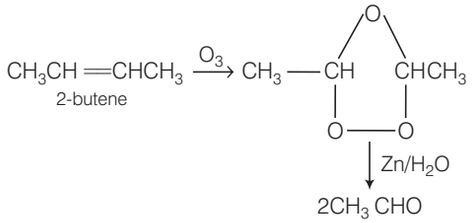
$\Rightarrow$ $C_nH_{2n} = 28\ u \Rightarrow n = 2$

Thus, the aldehyde comes out to be C_2H_4O or CH_3CHO. In order to identify an alkene, place 2 molecules of CH_3CHO with O–atom face to face.

Then, replace O atom by doube bond.



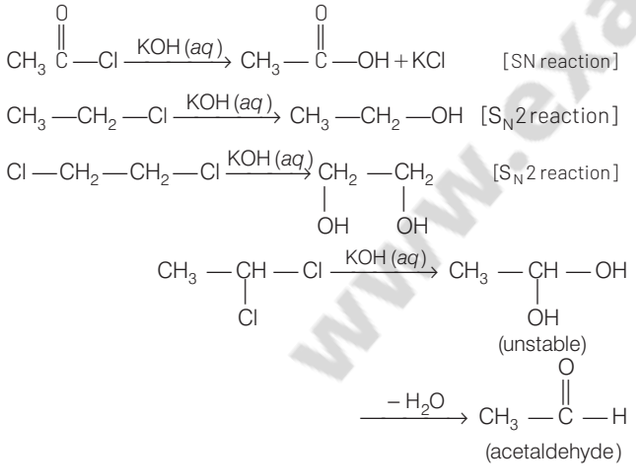
Hence,



144 Which of the following on heating with aqueous KOH, produces acetaldehyde? **[AIEEE 2009]**

(a) CH_3COCl (b) CH_3CH_2Cl (c) CH_2ClCH_2Cl (d) CH_3CHCl_2

Ans. ***(d)***



145 In Cannizzaro reaction given below

$$2PhCHO \xrightarrow{OH^{\ominus}} PhCH_2OH + PhCO_2^{\ominus}$$

the slowest step is **[AIEEE 2009]**

(a) the attack of $:OH^{\ominus}$ at the carboxyl group

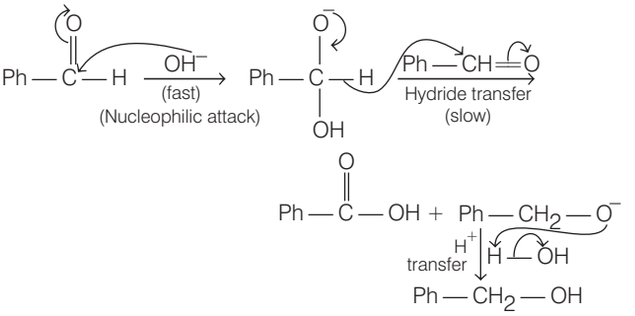
(b) the transfer of hydride to the carbonyl group

(c) the abstraction of proton from the carboxylic group

(d) the deprotonation of $PhCH_2OH$

Ans. ***(b)***

In Cannizaro reaction, the transfer of H^- to a carbonyl group is a slowest step of the reaction and hence, it is a rate determining step of the reaction.



146 The increasing order of the rate of HCN addition to compounds A-D is **[AIEEE 2006]**

(A) HCHO (B) CH_3COCH_3

(C) $PhCOCH_3$ (D) PhCOPh

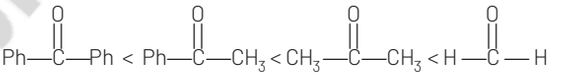
(a) A < B < C < D (b) D < B < C < A

(c) D < C < B < A (d) C < D < B < A

Ans. ***(c)***

Addition of HCN is a nucleophilic reaction. Greater the electron deficiency of C atom of carbonyl group, higher the rate of reaction.

Hence,



147 The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is **[AIEEE 2005]**

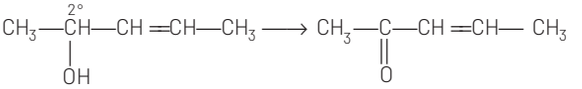
(a) pyridinium chloro-chromate

(b) chromic anhydride in glacial acetic acid

(c) acidic dichromate

(d) acidic permanganate

Ans. ***(b)***



Only suitable reagent is chromic anhydride in glacial acetic acid. Other will also effect (C = C) bond.

148 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid? **[AIEEE 2004]**

(a) Phenol (b) Benzaldehyde

(c) Butanal (d) Benzoic acid

Ans. ***(b)***

$$A + NaOH \rightarrow \text{alcohol} + \text{acid}$$

Thus, it is Cannizzaro reaction.

A is thus aldehyde without H at α-carbon.

(as C_6H_5CHO, HCHO)

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

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149 On vigorous oxidation by permangnate solution $(CH_3)_2C=CHCH_2CHO$ gives **[AIEEE 2002]**

(a) $(CH_3)_2CO$ and $OHCCH_2CHO$

(b) $(CH_3)_2\underset{|}{\overset{OH}{C}}-\underset{|}{\overset{OH}{CH}}CH_2CHO$

(c) $(CH_3)_2CO$ and $OHCCH_2COOH$

(d) $(CH_3)_2CO$ and $CH_2(COOH)_2$

Ans. ***(d)***

$C=C$ bond is cleaved and oxidised to —COOH,—CHO group is also oxidised to —COOH.

$$(CH_3)_2C=CHCH_2CHO \longrightarrow (CH_3)_2C=O + HOOC-CH_2-COOH$$

TOPIC 4
Carboxylic Acids

150 In the following sequence of reactions a compound *A*, (molecular formula $C_6H_{12}O_2$) with a straight chain structure gives a C_4 carboxylic acid. *A* is

$$A \xrightarrow[H_3O^+]{LiAlH_4} B \xrightarrow{\text{Oxidation}} C_4 \text{ carboxylic acid}$$

[2021, 01 Sep Shift-II]

(a) $CH_3-CH_2-COO-CH_2-CH_2-CH_3$

(b) $CH_3-CH_2-\underset{OH}{\underset{|}{C}}H-CH_2-O-CH=CH_2$

(c) $CH_3-CH_2-CH_2-COO-CH_2-CH_3$

(d) $CH_3-CH_2-CH_2-O-CH=CH-CH_2-OH$

Ans. ***(c)***

Ethylbutanoate on reduction with $LiAlH_4$ and hydrolysis gives butanol and ethanol. Butanol on further oxidation gives butanoic acid which has four carbon atoms. The complete reaction is as follows

$$CH_3-CH_2-CH_2-\underset{O}{\overset{\|}{C}}-O-CH_2-CH_3$$

Ethylbutanoate (A)

$\downarrow$ $LiAlH_4$, H_3O^+

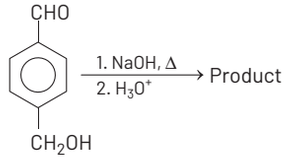
$$CH_3-CH_2-CH_2-CH_2-OH + CH_3-CH_2-OH$$

Butanol (*B*) Ethanol

$\downarrow$ Oxidation

$$CH_3-CH_2-CH_2-\underset{O}{\overset{\|}{C}}-OH$$

151 For the reaction given below.



The compound which is not formed as a product in the reaction is a **[2021, 31 Aug Shift-II]**

(a) compound with both alcohol and acid functional groups

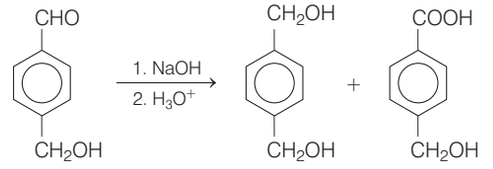
(b) monocarboxylic acid

(c) dicarboxylic acid

(d) diol

Ans. ***(c)***

In this reaction, one compound having alcohol and acid functional group and another one having two alcohol groups are formed.

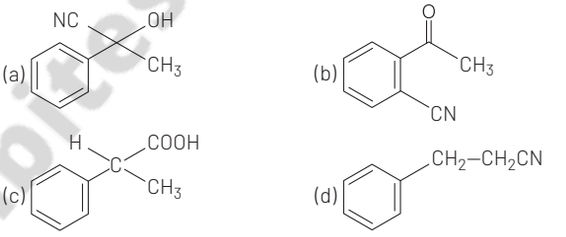


∴ Dicarboxylic acid not formed as a product.

152 The structure of product *C*, formed by the following sequence of reactions is

$$CH_3COOH + SOCl_2 \longrightarrow A \xrightarrow[AlCl_3]{\text{Benzene}} B \xrightarrow[-OH]{KCN} C$$

[2021, 31 Aug Shift-I]

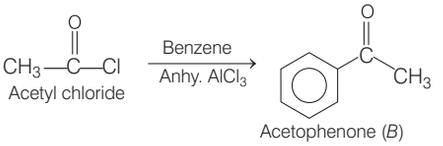


Ans. ***(a)***

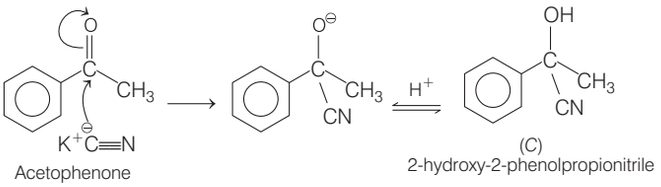
Acetic acid on reaction with $SOCl_2$ gives acetyl chloride (*A*).

$$\underset{\text{Acetic acid}}{H_3C-COOH} \xrightarrow{SOCl_2} \underset{\text{Acetyl chloride (A)}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl}$$

Acetyl chloride undergoes Friedel-Craft acylation in presence of anhyd. $AlCl_3$ and benzene to form acetophenone (*B*).



Acetophenone reacts with KCN to give (*C*) the final product, i.e. 2-hydroxy-2-phenolpropionitrile.



Hence, correct option is (a).

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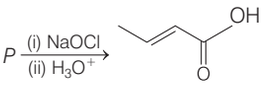
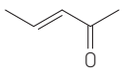
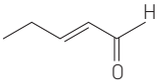
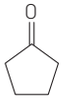
153 The structure of the starting compound *P* used in the reaction given below is **[2021, 27 Aug Shift-I]**



(a) 

(b) 

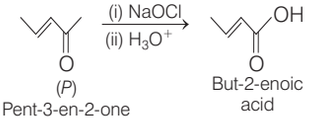
(c)

(d) 

Ans. ***(a)***

Sodium hypochlorite (NaOCl) is a strong oxidising agent that will convert ketone to carboxylic acid.

Since, product is carboxylic acid, therefore reactant (*P*) would be ketone.



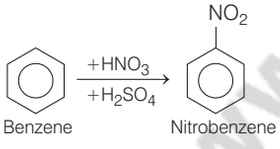
154 The correct sequential addition of reagents in the preparation of 3-nitrobenzoic acid from benzene is **[2021, 26 Aug Shift-I]**

(a) Br_2 /$AlBr_3$, HNO_3 /H_2SO_4, Mg /ether, CO_2, H_3O^+
(b) Br_2 / $AlBr_3$, NaCN, H_3O^+, HNO_3 / H_2SO_4
(c) Br_2 /$AlBr_3$, HNO_3 /H_2SO_4, NaCN, H_3O^+
(d) HNO_3 /H_2SO_4, Br_2 / $AlBr_3$, Mg/ether, CO_2, H_3O^+

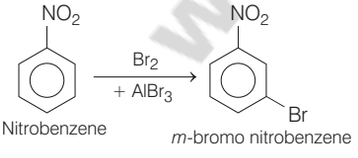
Ans. ***(d)***

The preparation of 3-nitrobenzoic acid from benzene is as follows

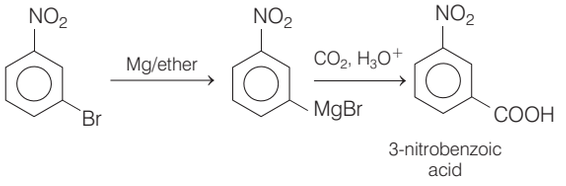
- Nitration of benzene



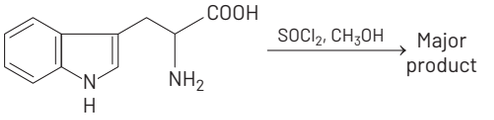
- Electrophilic substitution of nitrobenzene

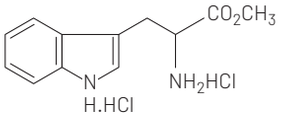


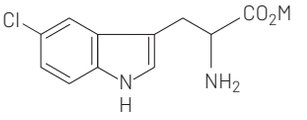
- m-bromo nitrobenzene is converted to 3-nitrobenzoic acid.

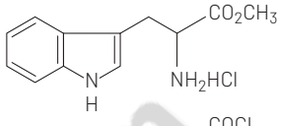


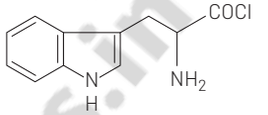
155 The major product formed in the following reaction is **[2021, 26 Aug Shift-I]**



(a) 

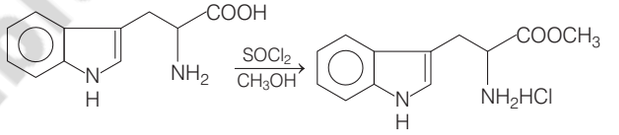
(b) 

(c) 

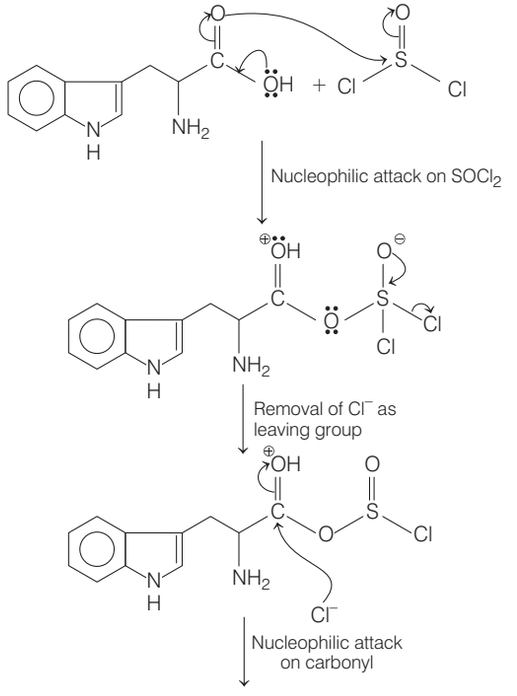
(d) 

Ans. ***(c)***

Esterification of carboxylic group (—COOH) take place in presence of $SOCl_2$ and CH_3OH has as follows



Mechanism



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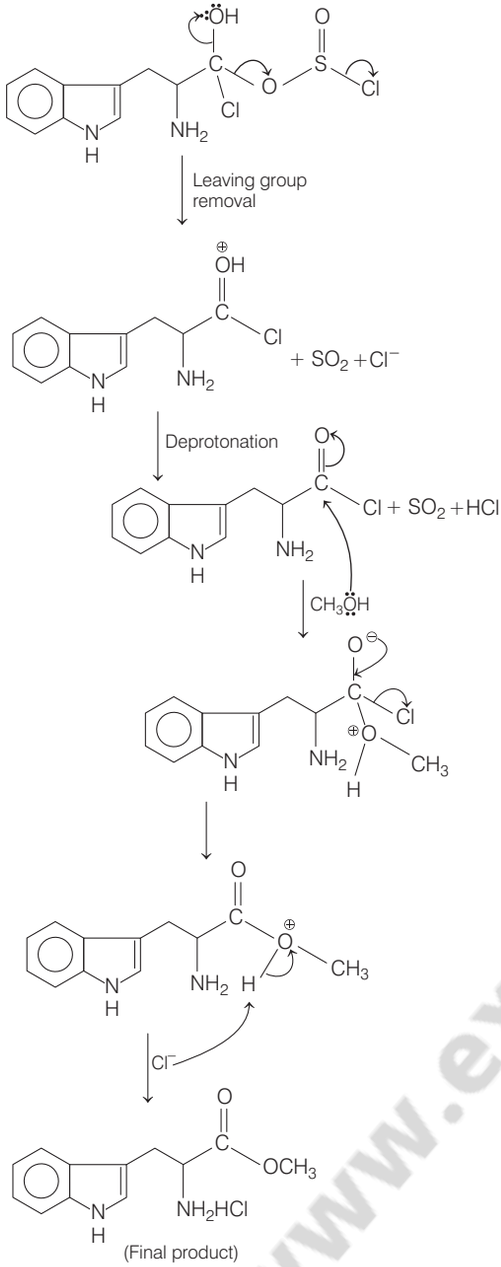
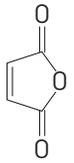


156



(Maleic anhydride)

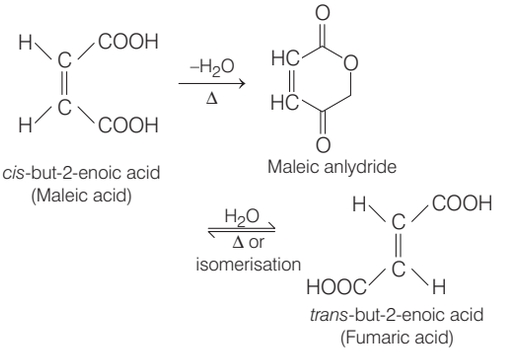
Maleic anhydride can be prepared by

[2021, 25 July Shift-II]

(a) heating *trans*-but-2-enedioic acid
(b) heating *cis*-but-2-enedioic acid
(c) treating *cis*-but-2-enedioic acid with alcohol and acid
(d) treating *trans*-but-2-enedioic acid with alcohol and acid

Ans. ***(b)***

Maleic acid is an organic compound that is a dicarboxylic acid. It mainly used as a precursor to fumaric acid, and relative to its parent maleic anhydride. Maleic anhydride can be prepared by heating *cis*-but-2-enedioic acid.



157 Which one of the following compounds will liberate CO_2, when treated with $NaHCO_3$? **[2021, 25 July Shift-I]**

(a) $(CH_3)_3\overset{\oplus}{N}H\overset{\ominus}{Cl}$ (b) $(CH_3)_3\overset{\oplus\ominus}{N}OH$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ (d) CH_3NH_2

Ans. ***(a)***

Compound (*A*), reacts with sodium bicarbonate to form carbonic acid which further dissociate to liberate CO_2 effervescence.

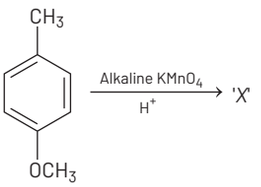
Bicarbonate test

$$(CH_3)_3\overset{\oplus}{N}HCl^- + NaHCO_3 \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3} + \underset{\text{Trimethyl-amine}}{(CH_3)_3N} + NaCl$$

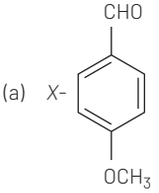
(Sodium bicarbonate)

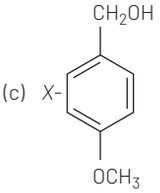
$$H_2CO_3 \longrightarrow \underset{\text{Carbon dioxide (effervescence)}}{CO_2} + H_2O$$

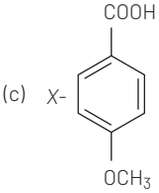
158

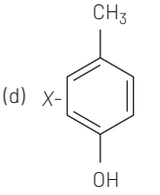


Considering the above chemical reaction, identify the product '*X*'. **[2021, 18 March Shift-I]**

(a) 

(c) 

(c) 

(d) 

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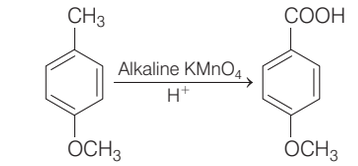
Ans. *(c)*

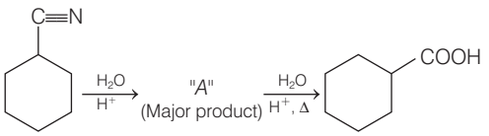
4-methoxy toluene in the presence of alkaline $KMnO_4$ to give 4-methoxy benzoic acid.

Chemical reaction is as follows :

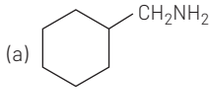


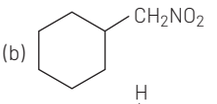
4-methoxy toluene (*X*) 4-methoxy benzoic acid

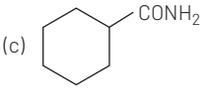
159

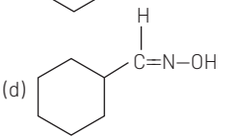


Consider the above chemical reaction and identify product "A" **[2021, 18 March Shift-I]**

(a) 

(b) 

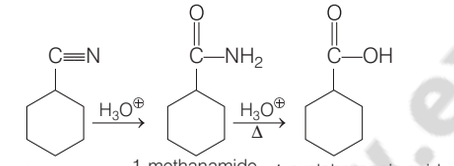
(c) 

(d) 

Ans. *(c)*

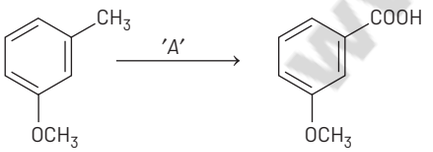
1-cyano cyclo hexane on complete hydrolysis gives 1-cyclo hexanoic acid. Intermediate 1- methanamide cyclohexane (*A*) is formed by partial hydrolysis.

Complete reaction is as follows



1-cyano cyclohexane; 1-methanamide cyclohexane 'A' Major product (Partial hydrolysis); 1-cyclohexanoic acid (Complete hydrolysis)

160



In the above reaction, the reagent '*A*' is **[2021, 16 March Shift-II]**

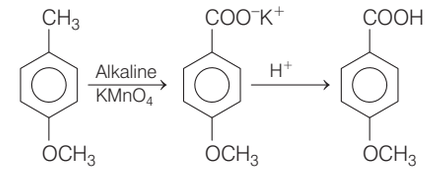
(a) $NaBH_4$, H_3O^+ (b) $LiAlH_4$

(c) Alkaline $KMNO_4$, H^+ (d) HCl, Zn - Hg

Ans. *(c)*

In the given reaction, *A* is alkaline $KMnO_4$, H^+.

Alkaline $KMnO_4$ /H^+ is a strong oxidising agent and oxidises alkyl benzene to benzoic acid. While $NaBH_4$, $LiAlH_4$ and Zn-Hg/HCl are reducing agent.



4-methoxy toluene 4-methoxy benzoate 4-methoxy benzoic acid

161 The number of compound(s) given below which contain(s) – COOH group is ..... .

(i) Sulphanilic acid

(ii) Picric acid

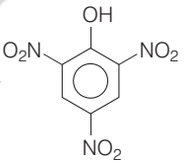
(iii) Aspirin

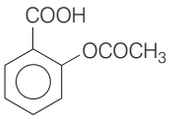
(iv) Ascorbic acid **[2021, 25 Feb Shift-II]**

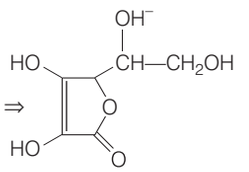
Ans. *(1)*

Structure of given compounds are as follows

(i) (Sulphanilic acid) ⇒

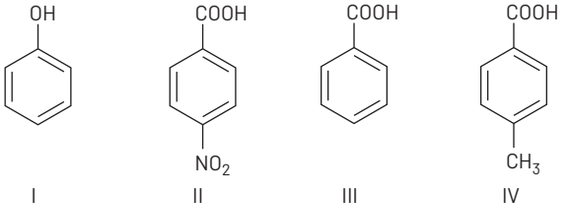
(ii) (Picric acid) ⇒ 

(iii) (Aspirin) ⇒ 

(iv) (Ascorbic acid) ⇒ 

Only one compound (iii) contains —COOH group.

162 The correct order of acid character of the following compounds is **[2021, 25 Feb Shift-II]**



I II III IV

Options

(a) I > II > III > IV

(b) III > II > I > IV

(c) II > III > IV > I

(d) IV > III > II > I

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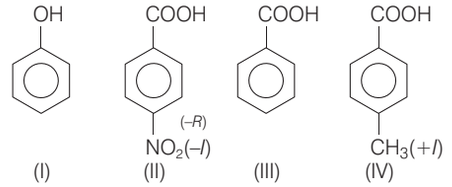
Ans. ***(c)***

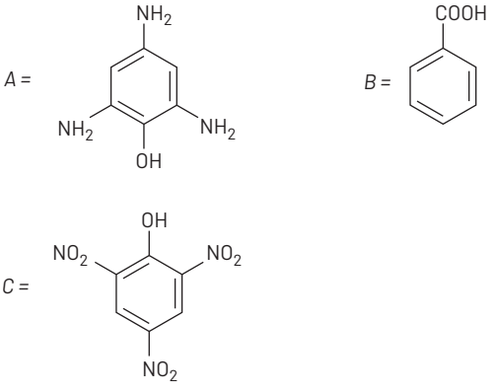


Acidity of phenol (I) is weaker than any carboxylic acid.

Electron withdrawing nature (–*R*, –*I*), of —NO_2 group at *para* position increases acidic strength of (II), whereas + *I* effect of —CH_3 group at *para* position decreases acidic strength of (IV).

So, the order of acid character is II > III > IV > I.

163 Compound(s) which will liberate carbon dioxide with sodium bicarbonate solution is/are **[2021, 25 Feb Shift-I]**

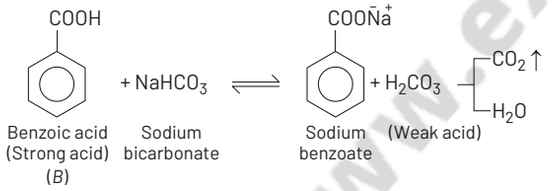


(a) *A* and *B* (b) *C* only

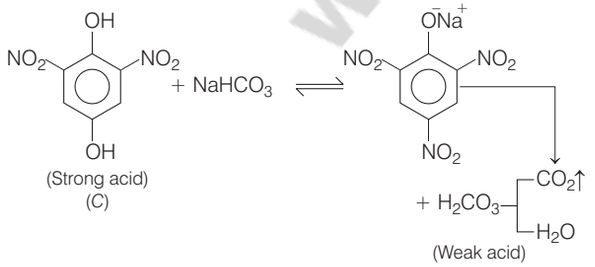
(c) *B* and *C* (d) *B* only

Ans. ***(c)***

The reactions of given compound with sodium bicarbonate solution are as follows

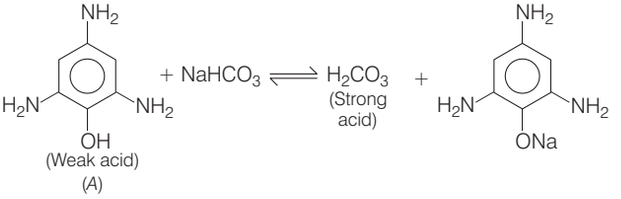


As H_2CO_3 is weak acid it dissociate to liberate CO_2 gas and H_2O.



Equilibrium favours forward direction and CO_2 is liberated. In the above two reactions, H_2CO_3 is comparatively weak acid.

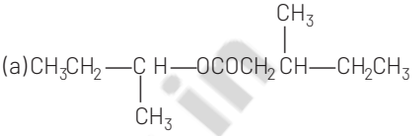
$\therefore$ CO_2 gas is liberated

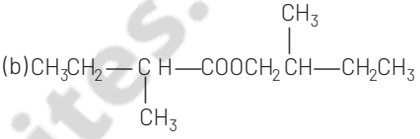


Equilibrium favours backward direction and CO_2 is not liberated.

Thus, only *B* and *C* will liberate carbon dioxide with sodium bicarbonate solution.

164 An organic compound [*A*], molecular formula $C_{10}H_{20}O_2$ was hydrolysed with dilute sulphuric acid to give a carboxylic acid [*B*] and an alcohol [*C*]. Oxidation of [*C*] with CrO_3 —H_2SO_4 produced [*B*]. Which of the following structures are not possible for [*A*]? **[2020, 3 Sep Shift-I]**



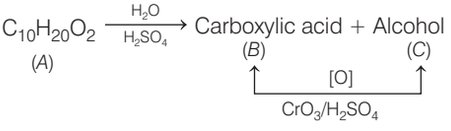


(c) $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$

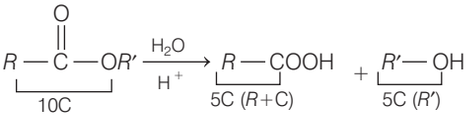
(d) $(CH_3)_3$—C—$COOCH_2C(CH_3)_3$

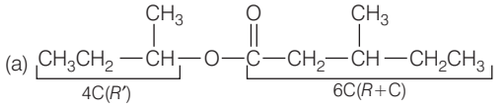
Ans. ***(a, c)***

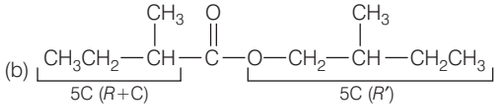
A can be written as : $(CH_3)_3C$—$COOCH_2C(CH_3)_3$]

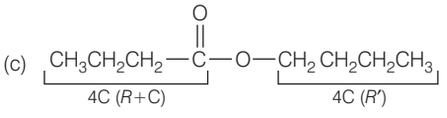


From the informations given, it is clear that *A* is an ester which contain 10 carbon atoms. Again, *C* on oxidation gives *B*. It indicates *B* and *C* contains equal number of carbon atom, i.e. each of *B* and *C* contains 5 carbon atom.









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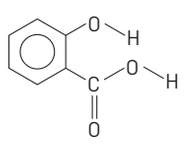
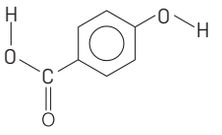
Note It is not having the molecular formula of $A(C_{10}H_{20}O_2)$. Its molecular formula $(C_8H_{16}O_2)$.

(d) $\underbrace{(CH_3)_3C-\overset{\overset{O}{\|}}{C}}_{5C\ (R+C)}-O=\underbrace{CH_2-C-(CH_3)_3}_{5C\ (R')}$

$\xrightarrow{H_3O^{\oplus}}$ $\underset{(B)}{(CH_3)_3C-COOH} + \underset{\uparrow [O]}{HO-CH_2-C(CH_3)_3}$ (C)

165 Consider the following molecules and statements related to them

(A)  (B) 

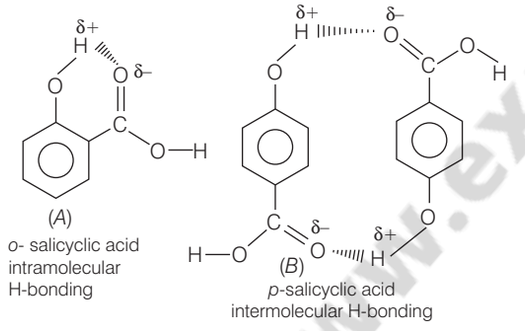
(I) (*B*) is more likely to be crystalline than (*A*).
(II) (*B*) has higher boiling point than (*A*).
(III) (*B*) dissolves more readily than (*A*) in water.
Identify the correct option from below :

[2020, 3 Sep Shift-II]

(a) (I) and (III) are true (b) Only (I) is true
(c) (II) and (III) are true (d) (I) and (II) are true

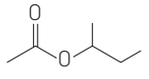
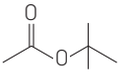
Ans. ***(c)***

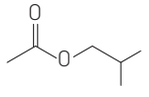
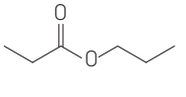
Given, molecules (*A*) and (*B*) undergoes intramolecular H-bonding and intermolecular H-bonding respectively. It is shown as follows :



Among the given statements, II and III are true whereas I is false. Corrected statement I, (*A*) is more likely to crystalline than (*B*).

166 An organic compound (*A*) (molecular formula $C_6H_{12}O_2$) was hydrolysed with dil. H_2SO_4 to give a carboxylic acid (*B*) and an alcohol (*C*). '*C*' gives white turbidity immediately when treated with anhydrous $ZnCl_2$ and conc. HCl. The organic compound (*A*) is **[2020, 4 Sep Shift-I]**

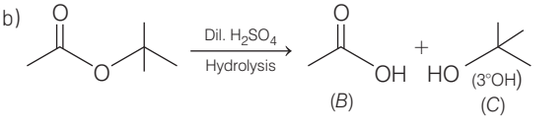
(a)  (b) 

(c)  (d) 

Ans. ***(b)***

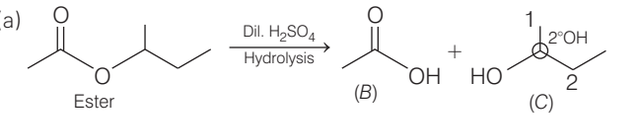
$ZnCl_2 + HCl \longrightarrow$ Lucas reagent

(*C*) give precipitate with Lucas reagent (immediately ppt.). It mean *C* will be 3° alcohol So, according to the given hints option (b) fits the category.

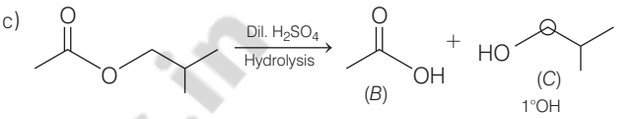
(b) 

is 3°OH. In 3°OH, it gives immediate ppt. then this is correct option.

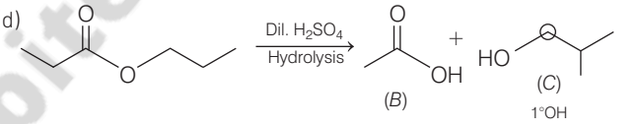
Explanation of other options are as follows :

(a) 

C is 2° alcohol, we want 3° alcohol then that this is incorrect option.

(c) 

C is 1°OH, it does not give ppt. immediately then that this is incorrect option.

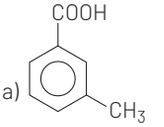
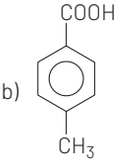
(d) 

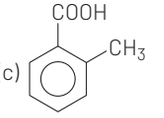
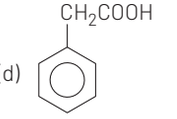
C is 1°OH that does not give test immdiately.

According to the question, compound

(*A*) gives carboxylic acid and alcohol on hydrolysis. So, *A* must be an ester.

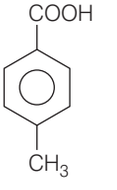
167 [*P*] on treatment with $Br_2/FeBr_3$ in CCl_4 produced a single isomer $C_8H_7O_2Br$ while heating [*P*] with sodalime gave toluene. The compound [*P*] is **[2020, 4 Sep Shift-I]**

(a)  (b) 

(c)  (d) 

Ans. ***(b)***

The compound [*P*] is 4-methyl benzoic acid.

Option (b) 

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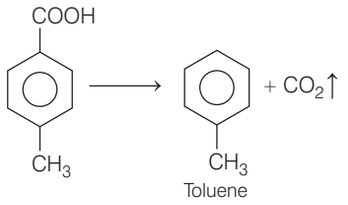
Here, —CH_3 group is *o*-and *p*-directing but *p*-position is already acquired by —COOH group. So, only one single product is formed.

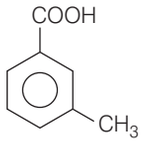
On treatment option (b) with sodalime, CO_2 gas is released COOH.



Toluene

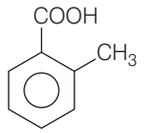
Other given options does not satisfy the condition.

Option (a)



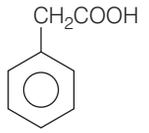
On promination 2 possible isomers will form.

Option (c)



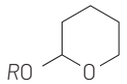
In respect of COOH, bromination occurs at *ortho* but in *ortho* is blocked by CH_3 and in respect of CH_3 bromination not possible.

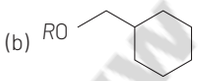
Option (d)

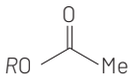


In respect of CH_2COOH bromination is done at *ortho* and *para*, then single isomer not possible.

168 Which of the following derivative of alcohols is unstable in an aqueous base? **[2020, 5 Sep Shift-I]**

(a) 

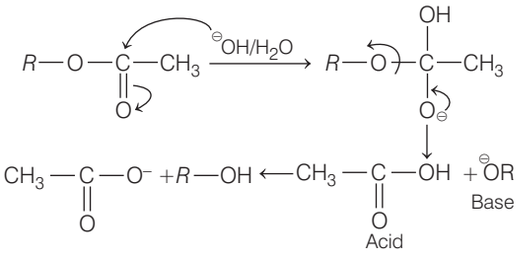
(b) 

(c) 

(d) $RO—CMe_3$

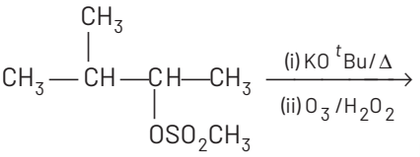
Ans. ***(c)***

Derivative of alcohols is unstable in an aqueous basic solution and undergoes hydrolysis to give alcohol and carboxylate.

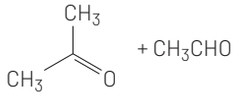


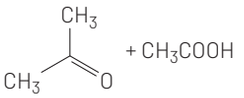
(It is a hydrolysis of ester in basic medium).

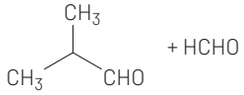
169 The major products of the following reaction are

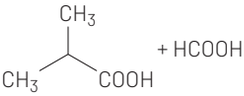


[2020, 6 Sep Shift-I]

(a) 

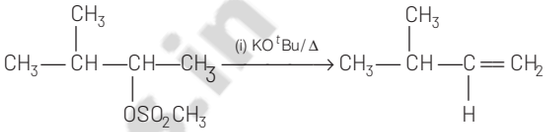
(b) 

(c) 

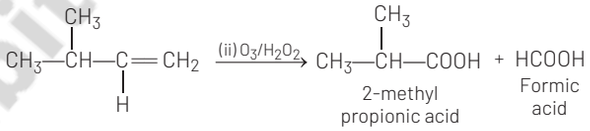
(d) 

Ans. ***(d)***

Tertiary butoxide is a bulky base, which favour elimination to form less substituted alkenes (Hofmann-product).



Now, alkene in presence of O_3/H_2O_2 undergoes oxidative ozonlysis to produce 2-methyl propionic acid and formic acid.



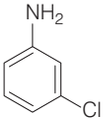
170 A solution of *m*-chloroaniline, *m*-chlorophenol and *m*-chlorobenzoic acid in ethyl acetate was extracted initially with a saturated solution of $NaHCO_3$ to give fraction *A*.

The left over organic phase was extracted with dilute NaOH solution to give fraction *B*. The final organic layer was labelled as fraction *C*. Fractions *A*, *B* and *C* contain respectively **[2020, 7 Jan Shift-I]**

(a) *m*-chlorobenzoic acid, *m*-chloroaniline and *m*-chlorophenol
(b) *m*-chlorophenol, *m*-chlorobenzoic acid and *m*-chloroaniline
(c) *m*-chlorobenzoic acid, *m*-chlorophenol and *m*-chloroaniline,
(d) *m*-chlorobenzoic acid and *m*-chlorophenol

Ans. ***(c)***

m-chloroaniline,



doesn't dissolve in $NaHCO_3$ or NaOH solutions because it has no considerable acidity and therefore can't form salt with bases.

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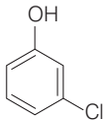
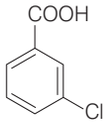
In *m*-chlorophenol;



which is substituted phenol is very weakly acidic which is sufficient to form their salt with NaOH. Therefore, these dissolve in dil. NaOH solution. But not acidic enough to form a salt with saturated $NaHCO_3$ solution.

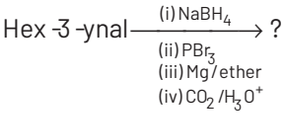
Carboxylic acids such as



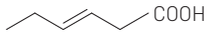
are strongly acidic. Their acidity is sufficient to form salt with *aq*.NaOH or *aq*. $NaHCO_3$.

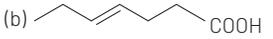
Therefore, *m*-chlorobenzoic acid (layer *A*) can be extracted by *aq*. $NaHCO_3$, then from the left over, *m*-chlorophenol (layer *B*) can be extracted by *aq*. NaOH. While the final organic layer (*C*) is of *m*-chloroaniline.

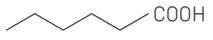
171 What is the product of following reaction?

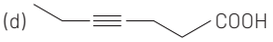


[2020, 7 Jan Shift-I]

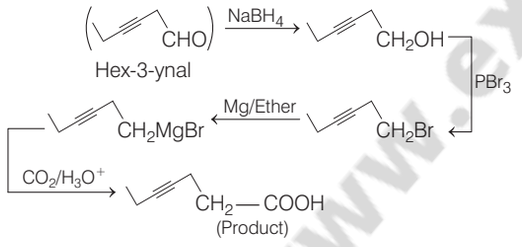
(a) 

(b) 

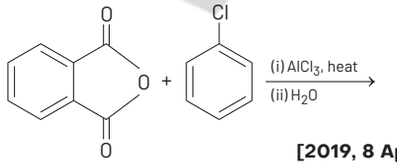
(c) 

(d) 

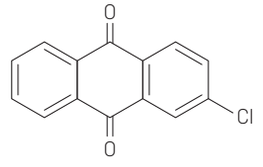
Ans. ***(d)***

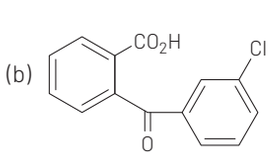


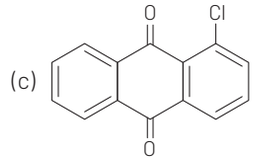
172 The major product of the following reaction is

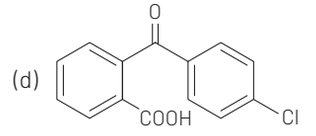


[2019, 8 April Shift-I]

(a) 

(b) 

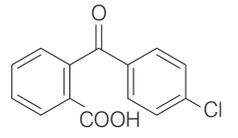
(c) 

(d) 

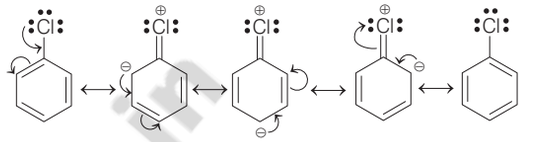
Ans. ***(d)***

The major product of the given reaction is (d).

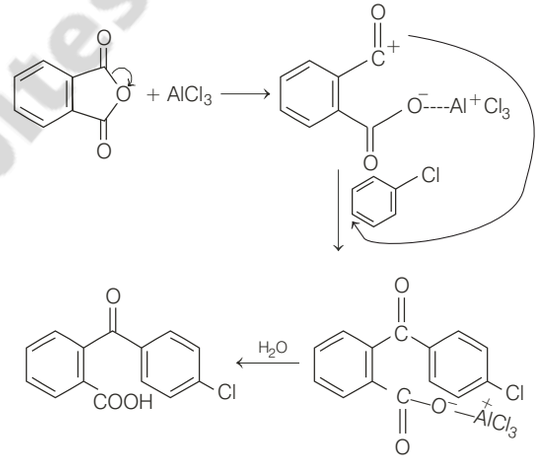
This reaction proceed *via* Friedel-Craft acylation. Here, —Cl group present on chlorobenzene is *ortho* and *para*-directing. It can be easily understood by resonating structures of chlorobenzene.



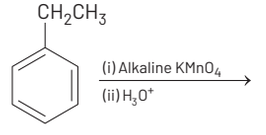
(d)



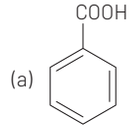
The given reaction proceed as follows :

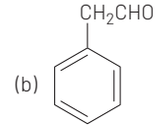


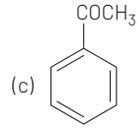
173 The major product of the following reaction is

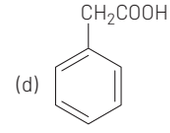


[2019, 9 April Shift-I]

(a) 

(b) 

(c) 

(d) 

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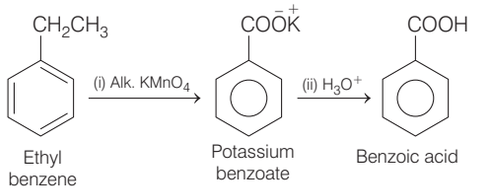
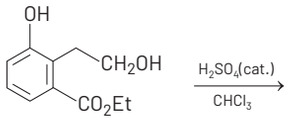
Ans. ***(a)***

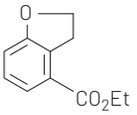
The major product of the given reaction is benzoic acid (C_6H_5COOH). On vigorous oxidation of alkyl benzene with acidic or alkaline $KMnO_4$, aromatic acids are obtained. During oxidation of alkyl benzene, the aromatic nucleus remains intact and the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.

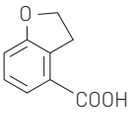


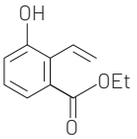
174 The major product of the following reaction is

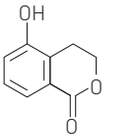


[2019, 9 April Shift-II]

(a) 

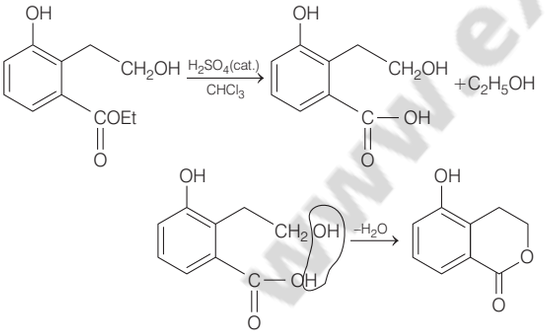
(b) 

(c) 

(d) 

Ans. ***(d)***

Given reaction involves acidic hydrolysis of esters followed by the intramolecular cyclisation. The chemical equation is as follows:



175 The correct decreasing order for acid strength is

(a) $FCH_2COOH > NCCH_2COOH > NO_2CH_2COOH > ClCH_2COOH$

(b) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$

(c) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$

(d) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

[2019, 9 Jan Shift-I]

Ans. ***(c)***

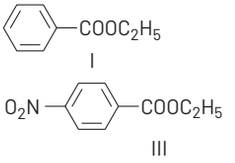
All the given compounds are α-monosubstituted acetic acid derivatives and the α-substitutions have been made by strong *–I* groups/atoms. More powerful the *– I* group, stronger will be the acid. *–I* power of different groups is as follows :

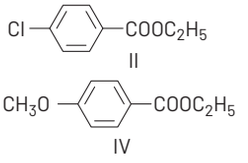
$$—NO_2 > —CN > —F > — Cl.$$

Thus, the correct decreasing order for acid strength is:

$NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$.

176 The decreasing order of ease of alkaline hydrolysis for the following esters is **[2019, 10 Jan Shift-I]**



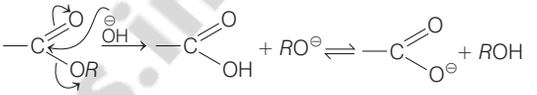


(a) III > II > IV > I (b) III > II > I > IV

(c) II > III > I > IV (d) IV > II > III > I

Ans. ***(b)***

Alkaline hydrolysis of an ester (carboxylic acid derivative) follows acyl S_N2 mechanism.



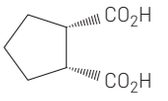
Rate of S_N2 mechanism depends on the polarity of group of —COO*R* group. Electron withdrawing group (*– R > – I*) increases the rate of S_N2 reaction whereas electron donating group (*+ R > + I*) decreases the rate of S_N2 reaction.

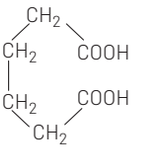
Here, the nature of functional groups attached *para* to the benzene ring are: $\underset{(-R)}{—NO_2} > \underset{(-I)}{— Cl} > \underset{(+R)}{— OCH_3}$

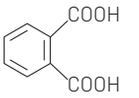
So, the order of hydrolysis will be, $\underset{(-R)}{III} > \underset{(-I)}{II} > I > \underset{(+R)}{IV}$

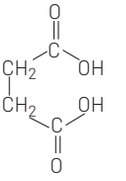
177 Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride?

[2019, 10 Jan Shift-I]

(a) 

(b) 

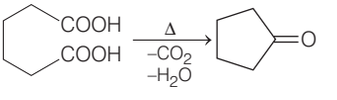
(c) 

(d) 

Ans. ***(b)***

Heating of $(CH_2)_4\begin{matrix}COOH\\COOH\end{matrix}$ (adipic acid) with

a dehydrating agent, decarboxylates (—CO_2) to give a ketone (cyclopentanone), not an anhydride.



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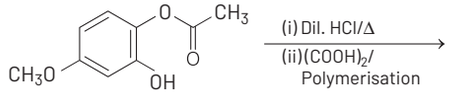
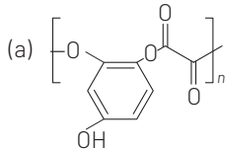
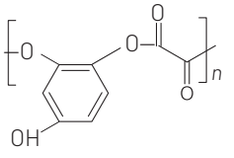
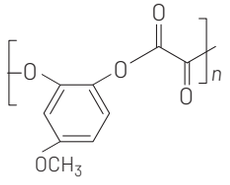
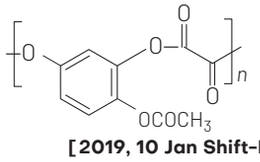
178 The major product of the following reaction is



(a) 

(b) 

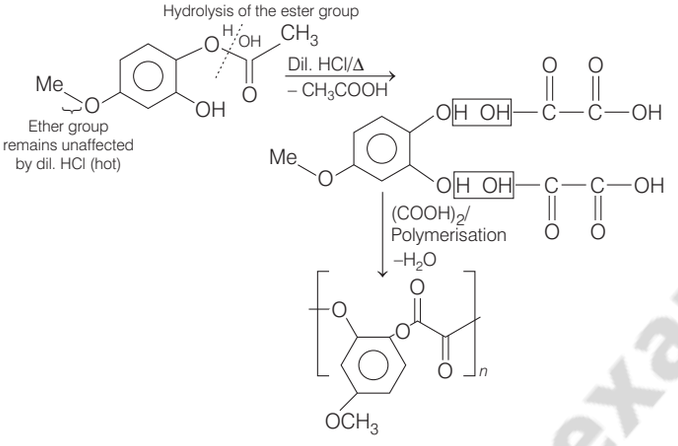
(c) 

(d) 

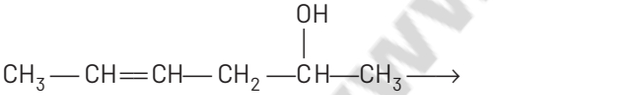
[2019, 10 Jan Shift-II]

Ans. ***(c)***

In the given reaction, ester get cleaved in presence of dil. HCl and readily forms alcohol. This alcohol on reaction with oxalic acid undergoes polymerisation reaction.



179 Which is the most suitable reagent for the following transformation ?



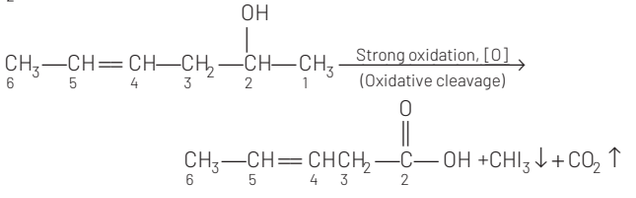
[2019, 10 Jan Shift-II]

(a) Tollen's reagent (b) I_2 / NaOH

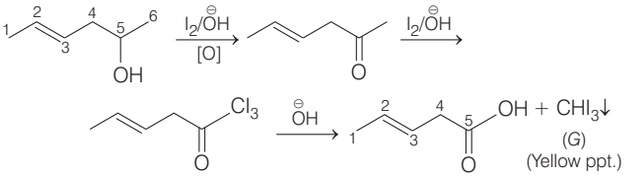
(c) Alkaline $KMnO_4$ (d) CrO_2Cl_2 / CS_2

Ans. ***(b)***

The most suitable reagent to carry out given transformation is I_2/NaOH

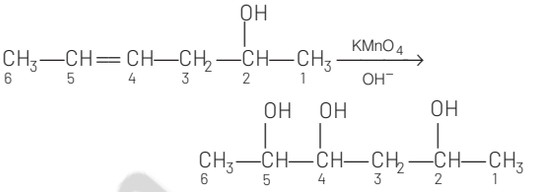


Here, the haloform reaction will give following reaction:



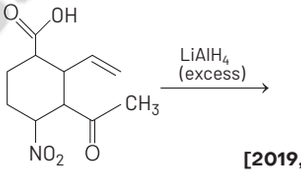
(i) Tollen's reagent ($AgNO_3 + NH_4OH$) is a mild oxidising agent. It does not react with —CH(OH)—CH_3 group (2°-alcohol).

(ii) Alkaline $KMnO_4$ cannot perform the oxidative cleavage, rather it will hydroxylate the C = C.

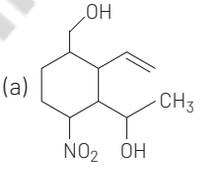


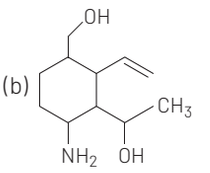
(iv) CrO_2Cl_2 / CS_2 will not react here.

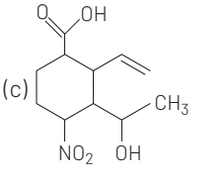
180 The major product obtained in the following reaction is

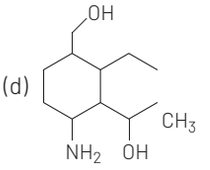


[2019, 11 Jan Shift-II]

(a) 

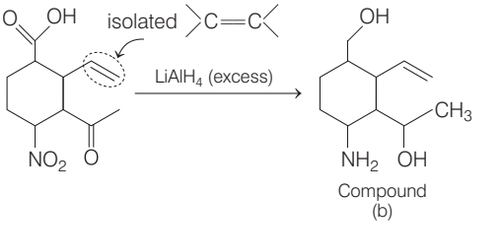
(b) 

(c) 

(d) 

Ans. ***(b)***

$LiAlH_4$ acts as a nucleophilic reducing agent that can reduce —COOH to $—CH_2OH$, —C(=O)— into —CH(OH)— and $—NO_2$ into $—NH_2$, but it cannot reduce isolated >C=C<



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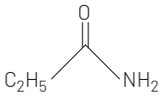
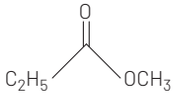
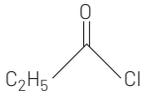
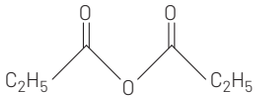
181 The increasing order of the reactivity of the following with $LiAlH_4$ is **[2019, 12 Jan Shift-II]**

(A) 

(B) 

(C) 

(D) 

(a) (A) < (B) < (D) < (C) (b) (A) < (B) < (C) < (D)

(c) (B) < (A) < (D) < (C) (d) (B) < (A) < (C) < (D)

Ans. ***(a)***

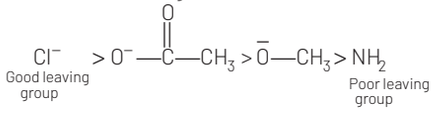
All the given compounds are acid derivatives, thus contain carbonyl group in them. $LiAlH_4$ reduces these compounds through nucleophilic substitution *via* addition elimination ($S_{N_A}E$) reaction. The rate of reaction depends upon the following factors :

(i) Size of alkyl group.

(ii) Steric hinderance around the > C = O group.

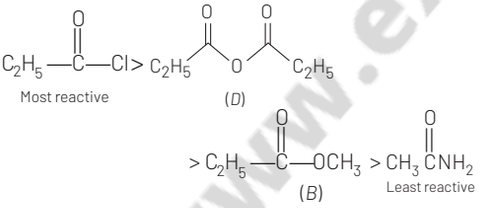
(iii) (+) ve charge on the C-atom of > C = O group.

The alkyl groups are more or less same in the given compounds. Thus, the reactivity order of given compounds depends upon 2nd and 3rd factor written above. The cumulative effect of these two factors results to leaving group ability (LGA) of the substituents in the following order :

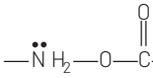


This leaving group ability (weak conjugate base) corresponds directly to the reactivity order.

Hence, the correct reactivity order is:



Note The *–I*-effect of –Cl and + *m*-effects of



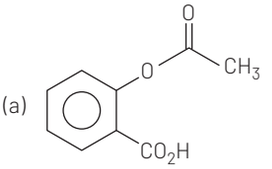
and — OCH_3 groups while attached to

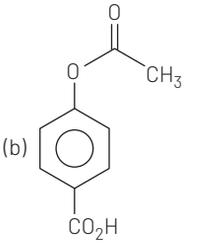
group to be reduced

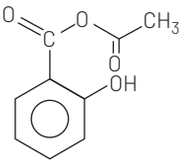
Also, add to the group leaving ability.

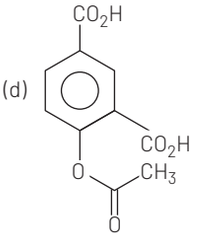
182 Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound *X* as the major product. *X* on treatment with $(CH_3CO)_2O$ in the presence of catalytic amount of H_2SO_4 produces:

[JEE Main 2018]

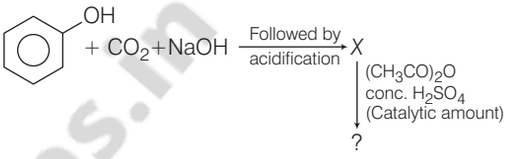
(a) 

(b) 

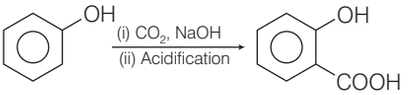
(c) 

(d) 

Ans. ***(a)***

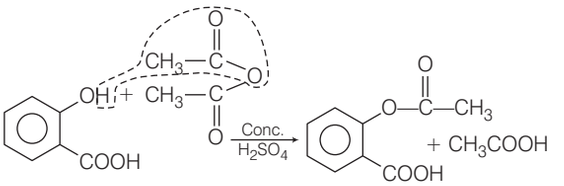


The very first reaction in the above road map looks like Kolbe's reaction which results to salicylic acid as



Salicylic acid (*X*)

The salicylic acid with acetic anhydride $[(CH_3CO)_2O]$ in the presence of catalytic amount of conc. H_2SO_4 undergoes acylation to produce aspirin as



Acetyl salicylic acid (Aspirin)

Aspirin is a non-narcotic analgesic (Pain killer).

183 In the following sequence of reaction,

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

The product C is **[JEE Main 2015]**

(a) C_6H_5COOH (b) $C_6H_5CH_3$ (c) $C_6H_5CH_2OH$ (d) C_6H_5CHO

Ans. ***(d)***

Toluene undergoes oxidation with $KMnO_4$, forms benzoic acid. In this conversion, alkyl part of toluene converts into carboxylic group. Further, benzoic acid reacts with thionyl chloride ($SOCl_2$) to give benzoyl chloride which upon reduction with H_2/Pd or $BaSO_4$ forms benzaldehyde (Rosenmund Reduction).

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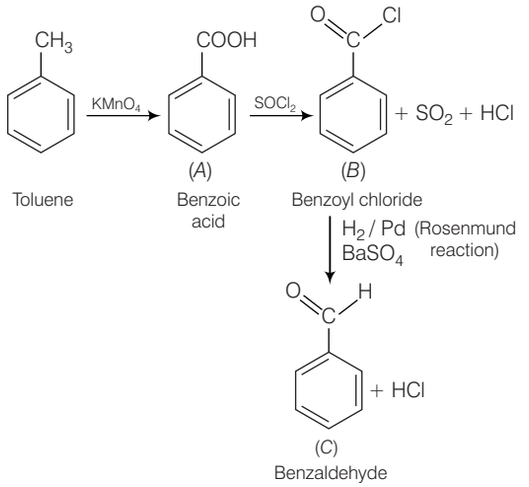
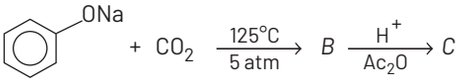
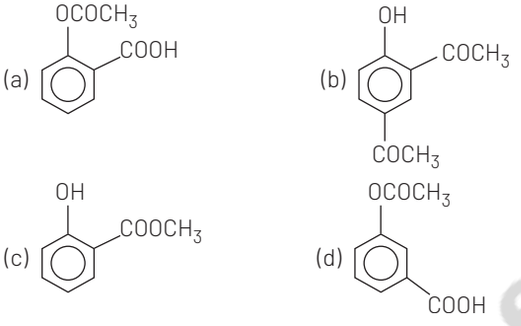
The conversion look like,



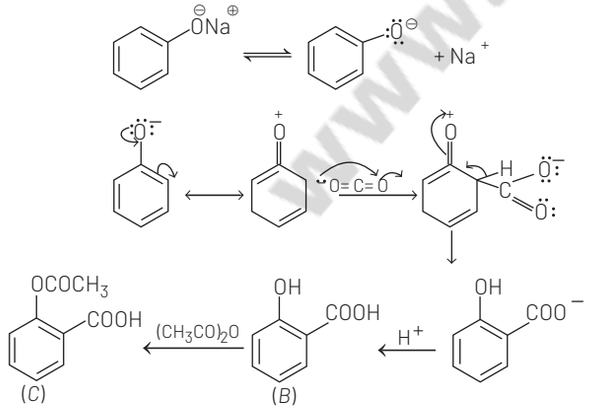
184 Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces *C*. **[JEE Main 2014]**



The major product *C* would be



Ans. ***(a)***



185 In the reaction,

$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{\text{alc. KOH}} C$$

the product *C* is **[JEE Main 2014]**

(a) acetaldehyde (b) acetylene
(c) ethylene (d) acetylchloride

Ans. ***(c)***

The complete series of reaction can be represented as

$$CH_3COOH \xrightarrow{LiAlH_4} \underset{(A)}{CH_3CH_2OH} \xrightarrow{PCl_5} CH_3CH_2Cl + POCl_3 + HCl$$

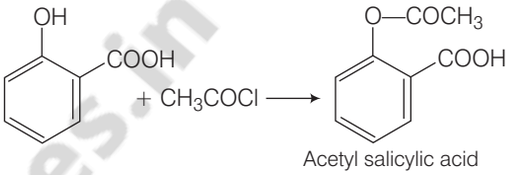
$$CH_3CH_2Cl \xrightarrow[\text{reaction}]{\text{elimination}} \text{alc.KOH} \Big\downarrow \quad CH_2{=}CH_2 \quad (C)$$

186 Aspirin is known as **[AIEEE 2012]**

(a) acetyl salicylic acid (b) phenyl salicylate
(c) acetyl salicylate (d) methyl salicylic acid

Ans. ***(a)***

Aspirin is acetyl derivative of salicylic acid.



187 Which of the following reagents may be used to distinguish between phenol and benzoic acid ? **[AIEEE 2011]**

(a) Aqueous NaOH (b) Tollen's reagent
(c) Molisch reagent (d) Neutral $FeCl_3$

Ans. ***(d)***

	Reagent	Phenol	Benzoic acid	Conclusion
(a)	Aqueous NaOH	Salt formation	Salt formation	No specific colour change
(b)	Tollen's reagent	No effect	No effect	
(c)	Molisch reagent	No effect	No effect	
(d)	Neutral $FeCl_3$	Violet colour	Buff-coloured precipitate	Thus, $FeCl_3$ can be used to make distinction

188 The strongest acid amongst the following compounds is **[AIEEE 2011]**

(a) CH_3COOH (b) $HCOOH$
(c) $CH_3CH_2CH(Cl)CO_2H$ (d) $ClCH_2CH_2CH_2COOH$

Ans. ***(c)***

– *I* effect exerting (electron withdrawing) groups increases the acidic strength of an acid by withdrawing electron density towards itself, they weakning O—H bond and thus, the release of H^+ ion by an acid becomes easier.

Whereas +*I* effect excerting (e^- releasing) groups decreases the acidic strength by donating electron density to O-atom. Further, – *I* effect decreases with distance. Thus, the acidic strength of the given acids would be

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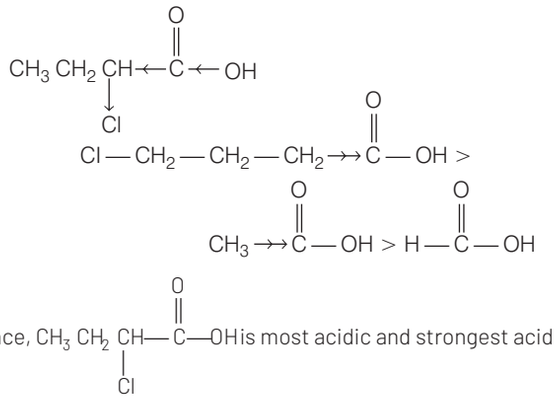


Hence, $CH_3CH_2\underset{Cl}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$ is most acidic and strongest acid than other given compounds.

189 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was **[AIEEE 2009]**

(a) CH_3OH (b) HCHO (c) CH_3COCH_3 (d) CH_3COOH

Ans. ***(d)***

$$\text{A liquid} + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{(Fruity smell)}}{\text{Compound}}$$

Fruity smell is the characteristic property of ester, thus the above reaction leads to the formation of ester.

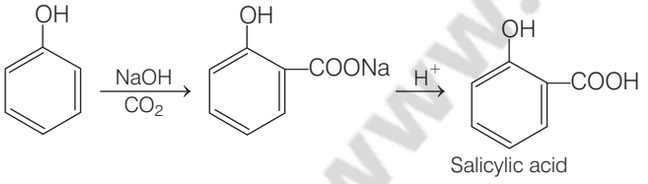
$$CH_3COOH + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Ethyl acetate (Fruity smell)}}{CH_3\overset{O}{\overset{\|}{C}}-OC_2H_5} + H_2O$$

This reaction is called esterification.

190 The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is **[AIEEE 2009]**

(a) benzoic acid (b) salicylaldehyde
(c) salicylic acid (d) phthalic acid

Ans. ***(c)***



Salicylic acid

The above reaction is called Kolbe's reaction.

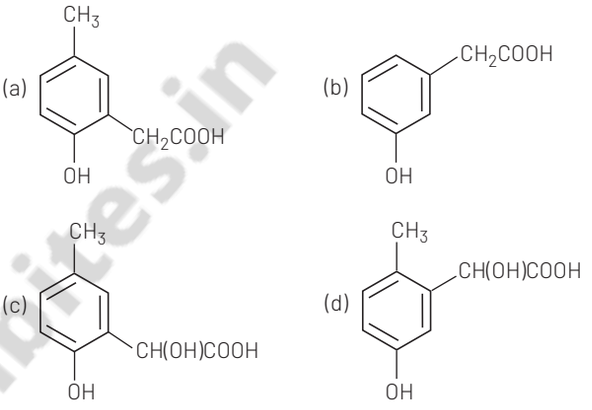
191 The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is **[AIEEE 2007]**

(a) benzophenone
(b) acetophenone
(c) benzoic acid
(d) benzyl alcohol

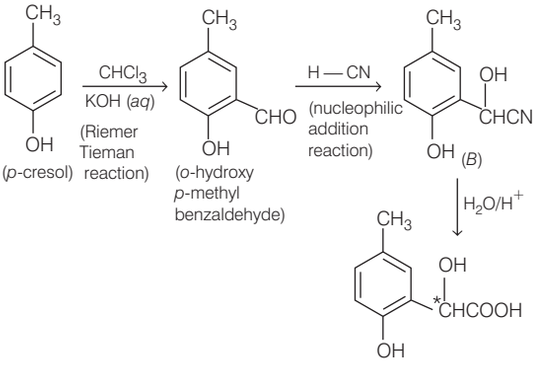
Ans. ***(c)***

Any aliphatic carbon with hydrogen attached to it, in combination with benzene ring, will be oxidised to benzoic acid by $KMnO_4$ / H^+.

192 *p*-cresol reacts with chloroform in alkaline medium to give the compound *A* which adds hydrogen cyanide to form the compound *B*. The latter, on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is **[AIEEE 2005]**



Ans. ***(c)***



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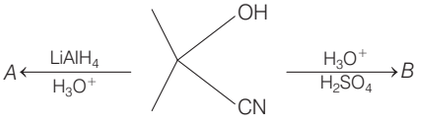
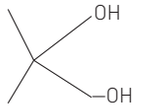
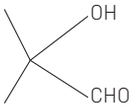
26

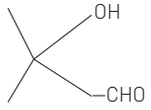
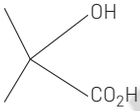
Organic Compounds Containing Nitrogen

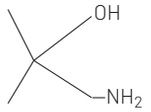
TOPIC 1
Aliphatic Amines

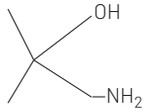
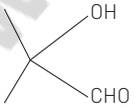
01 The major products *A* and *B* in the following set of reactions are **[2021, 31 Aug Shift-I]**



(a) *A* =  , *B* = 

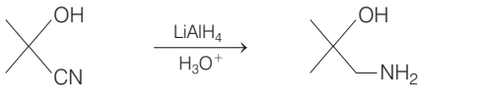
(b) *A* =  , *B* = 

(c) *A* =  , *B* =

(d) *A* =  , *B* = 

Ans. ***(c)***

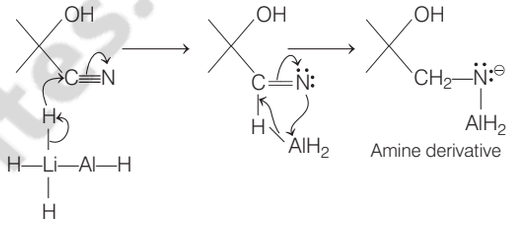
Nitriles can be converted to 1° amines by reaction with $LiAlH_4$.



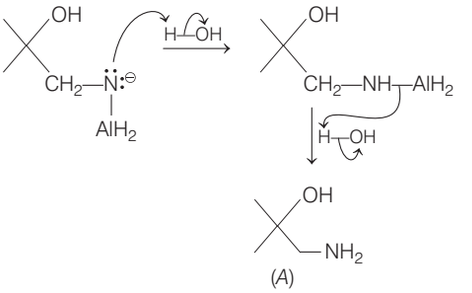
2-hydroxy-2-methyl propionitrile (*A*) — 1-amino-2-methylpropan-2-ol

Mechanism

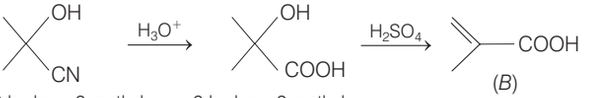
(i) Hydride nucleophile attacks the electrophilic carbon in nitrile to form imine anion.



(ii) Hydrolysis of amine derivative.

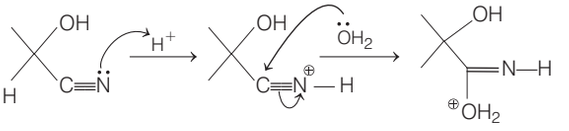


2-hydroxy-2-methyl propionitrile on acidic hydrolysis gives 2-hydroxy-2-methylpropionic acid.



2-hydroxy-2-methyl propionitrile — 2-hydroxy-2-methyl propionic acid

Mechanism



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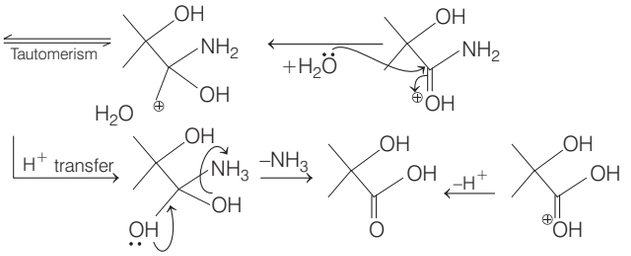
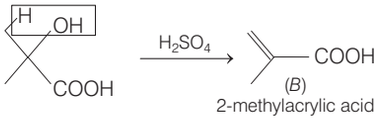
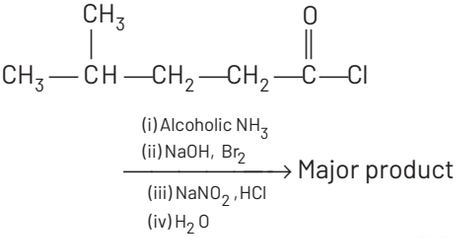


The last step of dehydration takes place in presence of H_2SO_4 to form 2-methylacrylic acid.

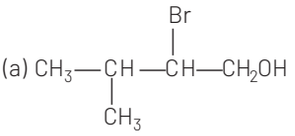
2-methylacrylic acid is the product (*B*).

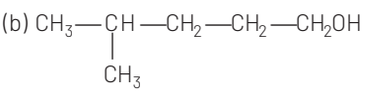


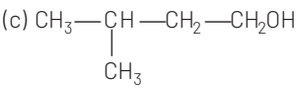
02 The major product of the following reaction is

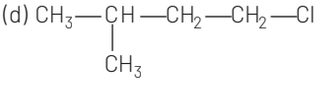


[2021, 27 Aug Shift-I]

(a) 

(b) 

(c) 

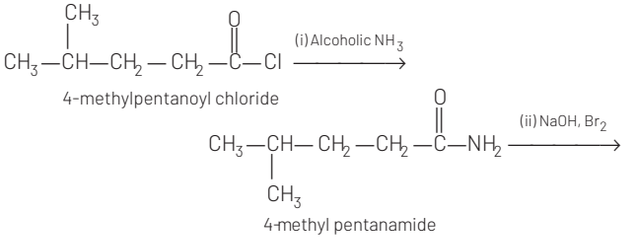
(d) 

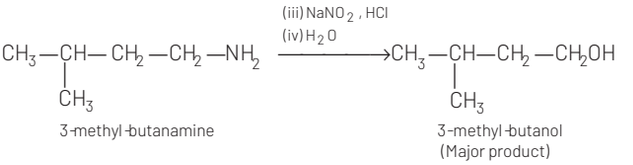
Ans. ***(c)***

In first step, ammonia reacts with ethanoyl chloride to give ethanamide and HCl. In the second step degradation of amide takes place that is known as Hoffmann's bromamide degradation reaction.

The third step is diazotisation, where an unstable diazonium salt is obtained, which further gives alcohol as a major product and alkene and alkyl halides.

The complete reaction is





03 Which of the following is not a correct statement for primary aliphatic amines? **[2021, 27 Aug Shift-I]**

(a) The intermolecular association in primary amines is less than the intermolecular association in secondary amines.

(b) Primary amines on treating with nitrous acid solution form corresponding alcohols except methyl amine.

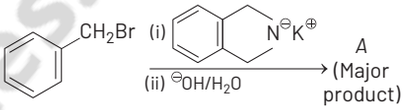
(c) Primary amines are less basic than the secondary amines.

(d) Primary amines can be prepared by the gabriel phthalimide synthesis.

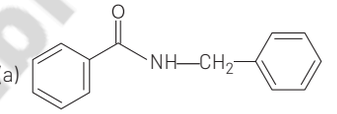
Ans. ***(a)***

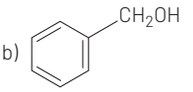
The intermolecular association is more in primary amines than in secondary amines as there is only one hydrogen atom available for formation of hydrogen bond in secondary amines, while primary amines has two hydrogen atoms. So, statement (a) is not correct.

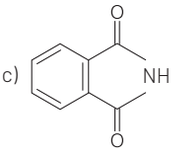
04 What is *A* in the following reaction?

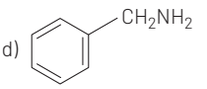


[2021, 27 July Shift-II]

(a) 

(b) 

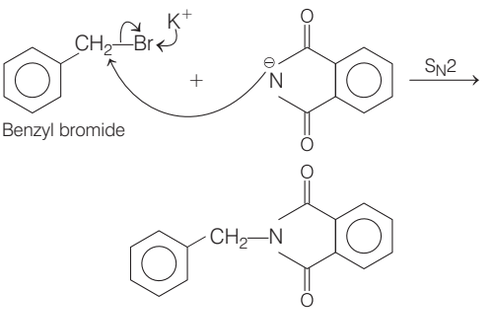
(c) 

(d) 

Ans. ***(d)***

Complete reaction is as follows :

(i) Removal of Br^- and formation of C—N bond *via* S_N2 mechanism.



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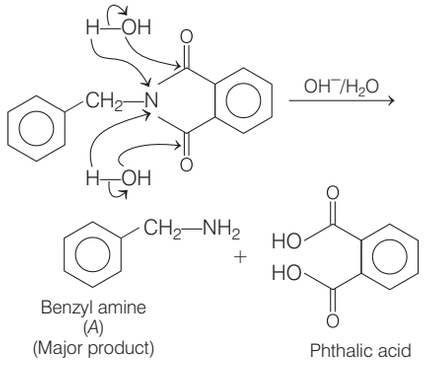
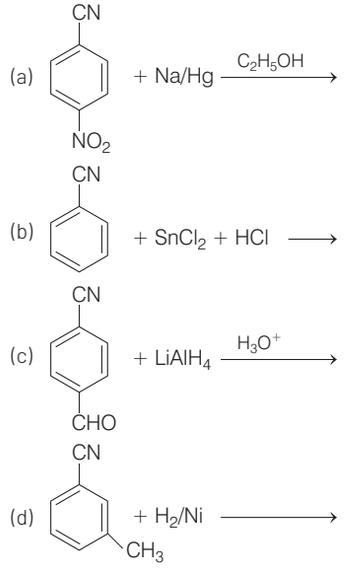
(ii) Hydrolysis process in basic medium Addition of OH^- ions for formation of phthalic acid and addition of H^+ ions for formation of benzyl amine.



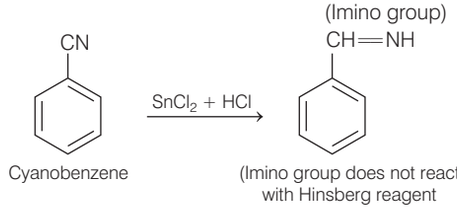
05 Which one of the products of the following reactions does not react with Hinsberg reagent to form sulphonamide? **[2021, 25 July Shift-I]**



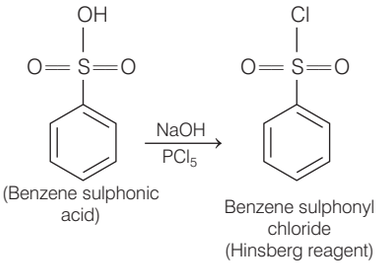
Ans. ***(b)***

Hinsberg reaction is a test for the detection of primary, secondary and tertiary amines. In this test, the amine is shaken well with Hinsberg reagent in the presence of aqueous alkali.

A reagent containing an aqueous sodium hydroxide solution and benzene sulphonyl chloride is added to a substrate. In reaction (b), imino group formed does not react with Hinsberg reagent.



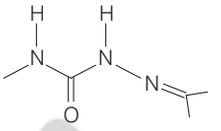
Product formed in all other reactions is a primary amine so, it gives Hinsberg reagent.



06 The number of nitrogen atoms in a semicarbazone molecule of acetone is ..... . **[2021, 20 July Shift-I]**

Ans. ***(3)***

Three nitrogen atoms are present as per structure below



Semicarbazone molecule of acetone

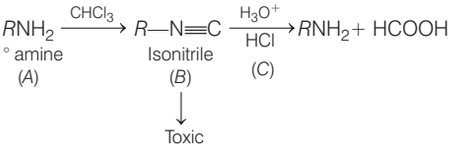
07 Compound *A* is converted to *B* on reaction with $CHCl_3$ and KOH. The compound *B* is toxic and can be decomposed by *C*. *A*, *B* and *C* respectively are **[2021, 20 July Shift-I]**

(a) primary amine, nitrile compound, conc. HCl
(b) secondary amine, isonitrile compound, conc. NaOH
(c) primary amine, isonitrile compound, conc. HCl
(d) secondary amine, nitrile compound, conc. NaOH

Ans. ***(c)***

Primary amine reacts in presence of chloroform gives isonitrile which is toxic in nature which further reacts in presence of HCl/H_3O^+ to give primary amine and acid.

Chemical reaction is as follows



Hence, *A*-primary amine, *B*-isonitrile compound and *C*-conc. HCl.

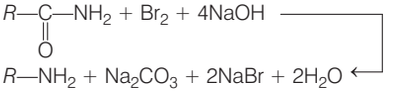
08 In the reaction of hypobromite with amide, the carbonyl carbon is lost as **[2021, 18 March Shift-II]**

(a) CO_3^{2-} (b) HCO_3^-
(c) CO_2 (d) CO

Ans. ***(a)***

Hypobromite transforms the primary amide to carbonic acid which further loses carbonyl carbon as CO_3^{2-}, yielding the amine product.

Chemical reaction is as follows



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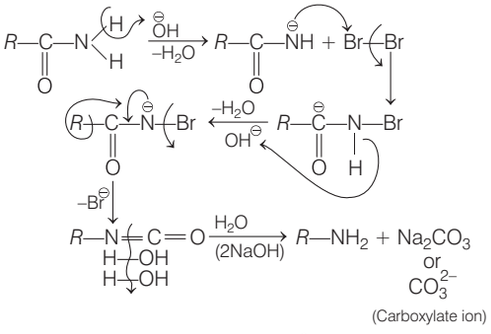
Mechanism



Thus, the carbonyl carbon is lost as CO_3^{2-} in the given reaction.

The complete reaction in ionic form looks like.

$$R\overset{\overset{O}{\|}}{C}NH_2 + 4BrO^- + 2H^+ \longrightarrow \underset{\text{(Amine)}}{RNH_2} + CO_3^{2-} + 4Br^- + \bar{O}H$$

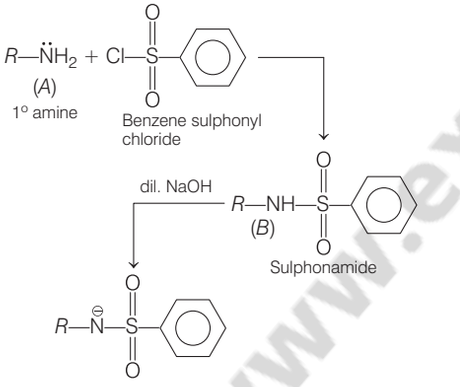
09 An organic compound "*A*" on treatment with benzene sulphonyl chloride gives compound *B*. *B* is soluble in dil. NaOH solution. Compound *A* is **[2021, 18 March Shift-II]**

(a) $C_6H_5-N-(CH_3)_2$ (b) $C_6H_5-NHCH_2CH_3$

(c) $C_6H_5-CH_2NHCH_3$ (d) $C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$

Ans. ***(d)***

Hinsberg reagent (benzene sulphonyl chloride) with 1º amine gives sulphonamide product i.e. N-ethylbenzene sulphonamide and it is soluble in dil. NaOH.



Hence, *A* is 1° amine i.e. $C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$

10 Primary, secondary and tertiary amines can be separated using **[2021, 17 March Shift-II]**

(a) *para*-toluene sulphonyl chloride

(b) chloroform and KOH

(c) benzene sulphonic acid

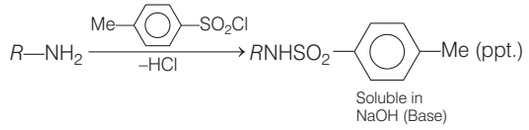
(d) acetyl amide

Ans. ***(a)***

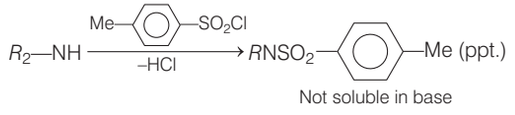
Primary, secondary and tertiary amines can be separated using *para*-toluene sulphonyl chloride. This test is known as Hinsberg test.

Reaction involved are as follows:

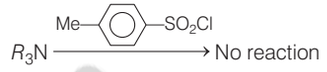
Primary (1°) amine Primary amines react with *para* toluene sulphonyl chloride to form a precipitate that is soluble in NaOH.



Secondary (2°) amine Secondary amines reacts with *para* toluene sulphonyl chloride to give a precipitate that is insoluble in NaOH.



Tertiary (3°) amine Tertiary amines do not react with *para* toluene.



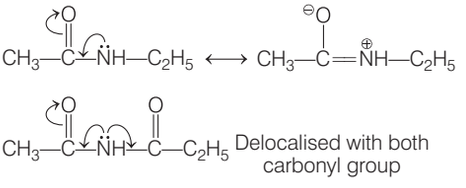
11 Which of the following is least basic? **[2021, 16 March Shift-II]**

(a) $(CH_3CO)\ddot{N}HC_2H_5$ (b) $(C_2H_5)_3\ddot{N}$

(c) $(CH_3CO)_2\ddot{N}H$ (d) $(C_2H_5)_2\ddot{N}H$

Ans. ***(c)***

Basic nature is directly proportional to electron releasing tendency. If lone pair is delocalised, electron density decreases and basic strength decreases.



So, there is delocalisation of electron in both options (a) and (c).

But it option (c) there is delocalisation of electron with both carbonyl group. Hence, it is weakest base.

There is a subtle interplay of the inductive effect, solvation effect and steric hinderance of the alkyl group, which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of ethyl substituted amines in aqueous solution is as follows

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

$\therefore (C_2H_5)_2\ddot{N}H$ is strong base.

12 Ammonolysis of alkyl halides followed by the treatment with NaOH solution can be used to prepare primary, secondary and tertiary amines. The purpose of NaOH in the reaction is **[2021, 16 March Shift-II]**

(a) to remove basic impurities

(b) to activate NH_3 used in the reaction

(c) to remove acidic impurities

(d) to increase the reactivity of alkyl halide

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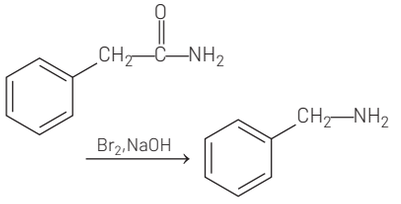
Ans. ***(c)***

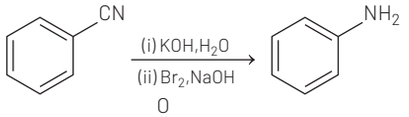
Ammonolysis of alkyl halides

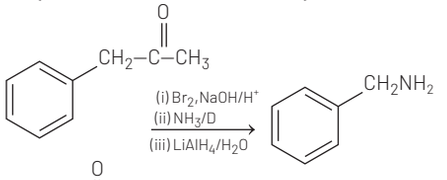
$$R\text{–}X \xrightarrow[-HX]{NH_3} R\text{—}NH_2 \xrightarrow[-HX]{R\text{—}X} R_2NH \xrightarrow[-HX]{R\text{—}X} R_3N \xrightarrow{RX} R_4\overset{\oplus}{N}X^{\ominus}$$

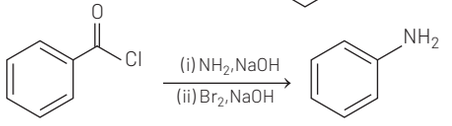
During the reaction HX (acid) is formed. Hence, we use NaOH to remove this acidic impurities.

13 Which of the following reaction does not involve Hoffmann bromamide degradation? **[2021, 16 March Shift-I]**

(a) 

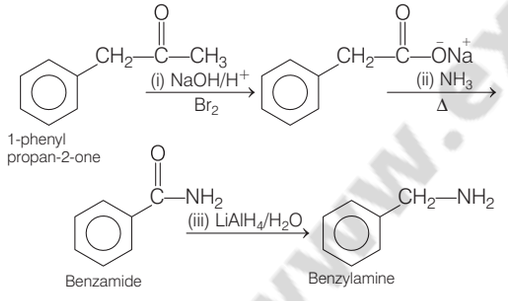
(b) 

(c) 

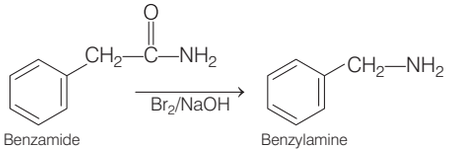
(d) 

Ans. ***(c)***

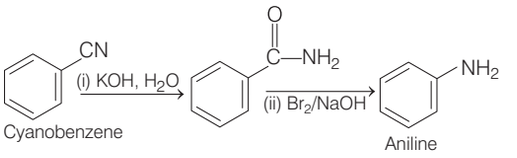
Methyl ketone gives haloform reaction to form carboxylic acid salt which on heating with NH_3 forms amide. Amide is reduced to amine by $LiAlH_4$.



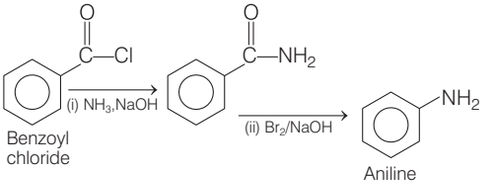
(a) Benzamide undergoes Hofmann bromamide degradation when treated with bromine and aqueous sodium hydroxide, to produces benzylamine.



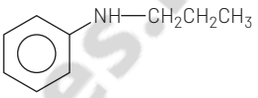
(b) Benzene nitrile undergoes alkaline hydrolysis to form acidamide which further give Hofmann bromamide degradation.



(d) Acid chloride undergoes nucleophilic substitution with NH_3 to form acid amide. Acid amide undergoes Hoffmann bromamide degradation.



14 An amine on reaction with benzene sulphonyl chloride produces a compound insoluble in alkaline solution. This amine can be prepared by ammonolysis of ethyl chloride. The correct structure of amine is **[2021, 26 Feb Shift-I]**

(a) 

(b) $CH_3CH_2NH_2$

(c) $CH_3CH_2CH_2NHCH_3$

(d) $CH_3CH_2CH_2\overset{H}{N}—CH_2CH_3$

Ans. ***(d)***

The amine on reaction with benzene sulphonyl chloride (Heisenberg reagent) produces a compound insoluble in alkali. It indicates the amine is a 2° amine. i.e. all options are possible except option (b) which is a 1° amine ($CH_3CH_2NH_2$).

As this 2° amine can be prepared by ammonolysis of ethyl chloride, the 2°-amine should have at least one ethyl (C_2H_5) group.

(a) Ph—NH—$CH_2CH_2CH_3$ does not have ethyl group.

(c) $CH_3CH_2CH_2$—NH—CH_3 does not have ethyl group.

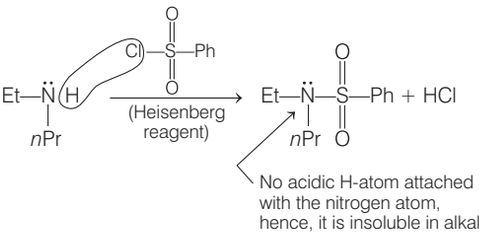
(d) $CH_3CH_2CH_2$—NH—CH_2CH_3 has one ethyl group.

So, option (d) is the correct answer.

Preparation $CH_3CH_2CH_2$—NH—CH_2CH_3 by ammonolysis of CH_3CH_2Cl

$$\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[-HCl]{NH_3} \underset{\text{Ethanamine (1°)}}{CH_3CH_2—NH_2} \xrightarrow{CH_3CH_2Cl\ (n\text{-propyl chloride})} \underset{\substack{\text{1-(N-ethyl)-propanamine}\\(2°)}}{CH_3CH_2—NH—CH_2CH_2CH_3}$$

Heisenberg test of CH_3CH_2—NH—$CH_2CH_2CH_3$ or Et—NH—*n*Pr



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15 The most appropriate reagent for conversion of C_2H_5CN into $CH_3CH_2CH_2NH_2$ is **[2020, 5 Sep Shift-I]**

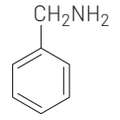
(a) $Na(CN)BH_3$ (b) $LiAlH_4$ (c) $NaBH_4$ (d) CaH_2

Ans. ***(b)***

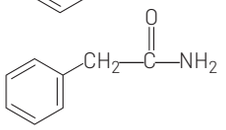
For the conversion of C_2H_5CN into $CH_3CH_2CH_2NH_2$, strong reducing agent is required among the given reducing agent. Strong reducing agent is $LiAlH_4$. It is the most appropriate reagent for this reduction.

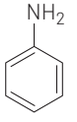
$$C_2H_5CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$$

16 Which of the following compounds can be prepared in good yield by Gabriel phthalimide synthesis? **[2020, 6 Sep Shift-II]**

(a) 

(b) $CH_3—CH_2—NHCH_3$

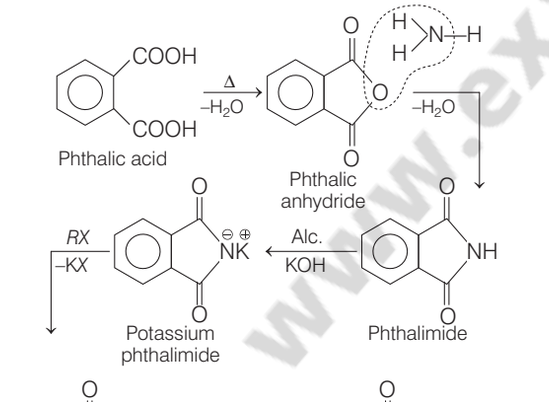
(c) 

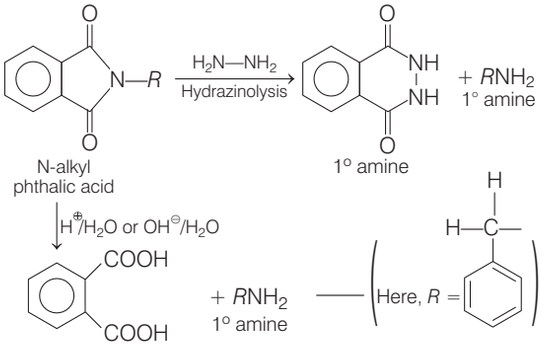
(d) 

Ans. ***(a)***

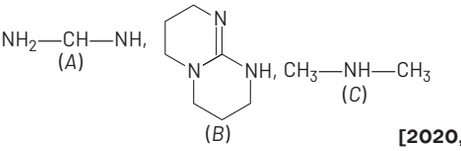
Gabriel phthalimide synthesis is used for the preparation of 1° aliphatic amine and 1° aromatic amine.

Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with *RX* followed by either alkaline hydrolysis or hydrazinolysis with hydrazine ($H_2N{\cdot}NH_2$) produces the corresponding 1° amine. 1° aromatic amine (except those containing EWG at *o*-and *p*-positions, e.g., $—NO_2$ group cannot be synthesised by this method because Ar*X* does not urdergo S_N reaction with anion formed by phthalimide.





17 The increasing order of pK_b for the following compounds will be :



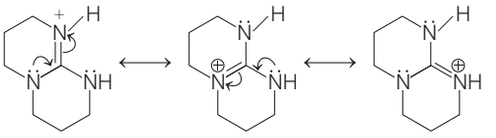
[2020, 7 Jan Shift-I]

(a) (*B*) < (*C*) < (*A*) (b) (*C*) < (*A*) < (*B*)

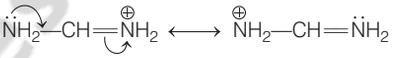
(c) (*A*) < (*B*) < (*C*) (d) (*B*) < (*A*) < (*C*)

Ans. ***(d)***

(*B*) is most basic because of high resonance stabilisation of its conjugate acid.



Among rest two compounds, $NH_2—CH=\overset{\cdot\cdot}{N}H$ (*A*) has higher basicity than $CH_3—NH—CH_3$ (*C*) because conjugate acid of (*B*) is resonance stabilised but conjugate acid of (*C*) is not resonance stabilised at all.

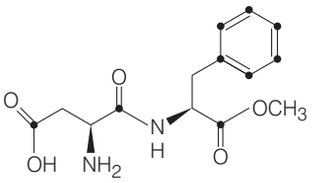


Hence, the correct order of basicity of the given compounds is, $B > A > C$. Stronger is the base, smaller will be its pK_b value. Thus, the increasing order of pK_b values is $B < A < C$.

18 The number of sp^2-hybridised carbons present in "aspartame" is ..... **[2020, 7 Jan Shift-II]**

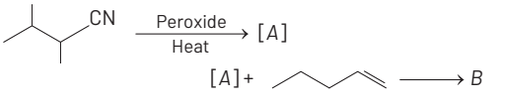
Ans. ***(9)***

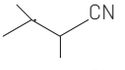
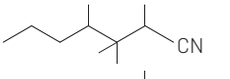
Structure of aspartame :

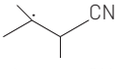
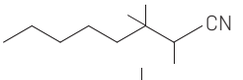


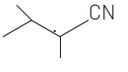
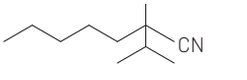
The 9 carbon atoms highlighted by the dark circle are sp^2-hybridised.

19 The major products *A* and *B* in the following reactions are : **[2020, 8 Jan Shift-I]**



(a) *A* =  and *B* = 

(b) *A* =  and *B* = 

(c) *A* =  and *B* = 

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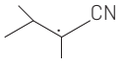
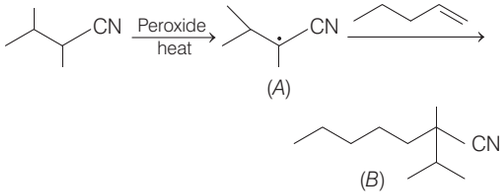
(d) *A* =  and *B* =

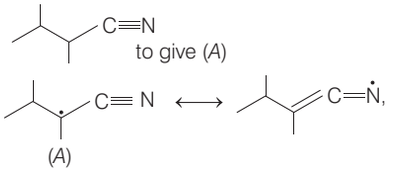
Ans. ***(c)***

The reaction is given as follows :

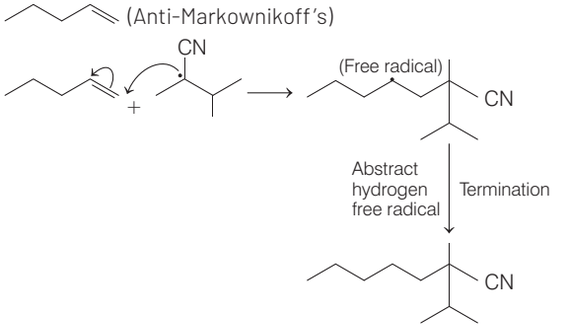


It can be proceed as :

Peroxide on heating give radicals which abstract hydrogen from



'*A*'which on addition to



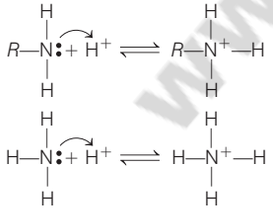
20 In the following compounds, the decreasing order of basic strength will be **[2019, 8 April Shift-I]**

(a) $C_2H_5NH_2 > NH_3 > (C_2H_5)_2NH$ (b) $(C_2H_5)_2NH > NH_3 > C_2H_5NH_2$

(c) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ (d) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

Ans. ***(c)***

Basic strength can be compared by the reaction of an alkanamine and ammonia with proton.

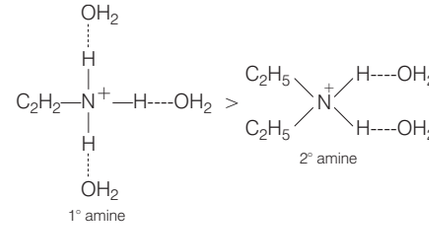


Basicity of an amine in aqueous solution depends upon the solubility of ammonium cation formed by accepting proton from water. The stability of ammonium cation depends upon the following factors.

(a) +*I*-effect (b) Steric effect (c) Solvation effect

In first case, on increasing the size of alkyl group +*I* effect increases and the positive charge of ammonium cation gets dispersed more easily, Therefore, order of basicity is 2º amine > 1º amine > ammonia.

In second case, substituted ammonium cation is also stabilised by solvation with water molecules. Greater the size of ion, lesser will be the solvation and less stabilised is the ion.



Considering both steric and solvation effect, it can be concluded that greater the number of H-atoms on the N-atom, greater will be the H-bonding and hence more stable is the ammonium cation. But in case of —C_2H_5 group, +*I*-effect predominates over H-bonding. Therefore, order is 2° amine > 1° amine > ammonia, i.e. $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$.

21 Which of the following amines can be prepared by Gabriel phthalimide reaction? **[2019, 8 April Shift-I]**

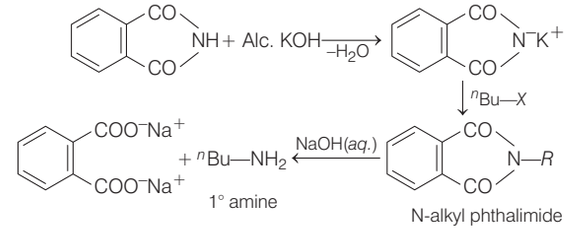
(a) *n* - butylamine (b) triethylamine

(c) *t*-butylamine (d) *neo* -pentylamine

Ans. ***(a)***

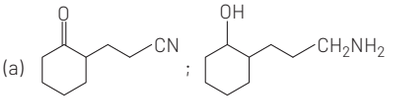
n- butylamine ($CH_3CH_2CH_2CH_2NH_2$) can be prepared by Gabriel phthalimide reaction. This method produces only primary amines without the traces of secondary or tertiary amines.

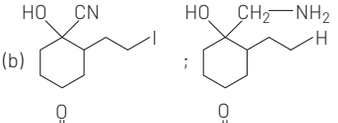
In this method, phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.

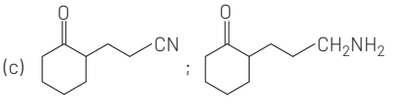


Triethylamine, *t*-butylamine and *neo*-pentylamine cannot be prepared by Gabriel phthalimide reaction.

22 The major products *A* and *B* for the following reactions are, respectively **[2019, 9 April Shift-II]**

(a) 

(b) 

(c) 

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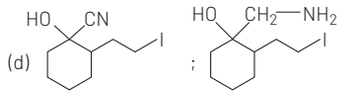
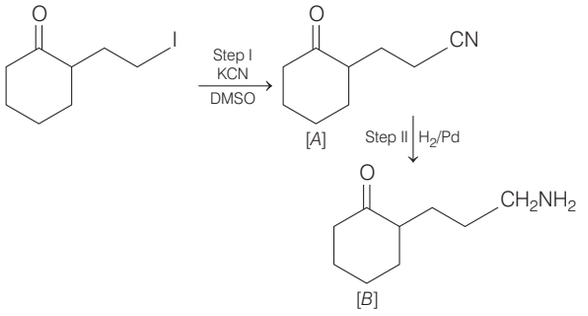
(d) 

Ans. ***(c)***



Step I involves the nucleophilic substitution reaction in which I (Iodine) is substituted by —CN group.

In step II, H_2/Pd reagent is used for reduction process. Here, —CN group reduces itself to $—CH_2NH_2$.

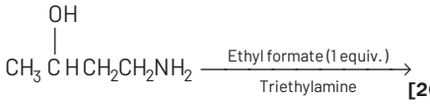
23 Hinsberg's reagent is **[2019, 9 April Shift-II]**

(a) $SOCl_2$ (b) C_6H_5COCl (c) $C_6H_5SO_2Cl$ (d) $(COCl)_2$

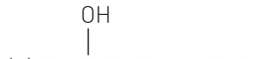
Ans. ***(c)***

Hinsberg's reagent is $C_6H_5SO_2Cl$ (benzene sulphonyl chloride). This reagent is used to distinguish between primary, secondary and tertiary amines.

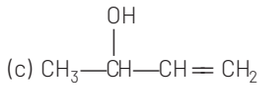
24 The major product of the following reaction is

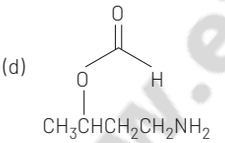


[2019, 10 April Shift-I]

(a) 

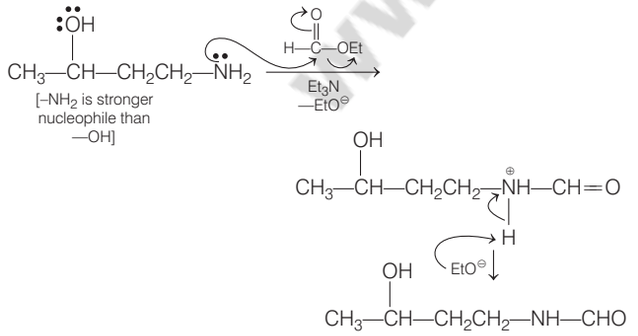
(b) $CH_3CH=CH—CH_2NH_2$

(c) 

(d) 

Ans. ***(a)***

The mechanism of the given reaction is as follows :



The basic mechanism of the reaction is acyl S_N2 because the nucleophile,

$CH_3(OH)CH_2CH_2NH_2$ attacks the sp^2 carbon of the ester (H —CO_2Et) and gets substituted.

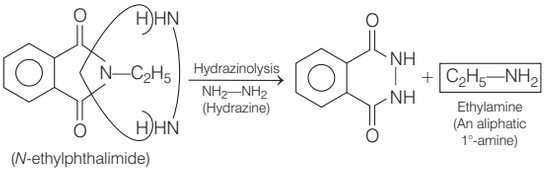
25 Ethylamine ($C_2H_5NH_2$) can be obtained from N-ethylphthalimide on treatment with **[2019, 10 April Shift-I]**

(a) $NaBH_4$ (b) NH_2NH_2

(c) H_2O (d) CaH_2

Ans. ***(b)***

The reaction for the production of ethylamine from *N*-ethylphthalimide can be takes place as follows:



(*N*-ethylphthalimide)

This reaction is the second step of Gabriel phthalimide synthesis for the preparation of aliphatic 1°-amines and amino acid. In this step concentrated alkali can also be used in place of hydrazine.

26 Which of the following is not a correct method of the preparation of benzylamine from cyanobenzene? **[2019, 10 April Shift-II]**

(a) H_2 / Ni

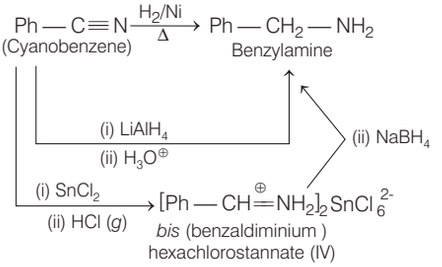
(b) (i) HCl/H_2O (ii) $NaBH_4$

(c) (i) $LiAlH_4$ (ii) H_3O^+

(d) (i) $SnCl_2$ + HCl(gas) (ii) $NaBH_4$

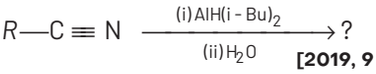
Ans. ***(b)***

The preparation of benzylamine from cyanobenzene using given reagents are as follows :



Thus, option (b) is incorrect.

27 The major product of following reaction is



[2019, 9 Jan Shift-I]

(a) *R*CHO (b) $RCONH_2$

(c) *R*COOH (d) RCH_2NH_2

Ans. ***(a)***

Key Idea DIBAL-H is diisobutyl aluminium hydride, $[(CH_3)_2CHCH_2]_2AlH$. It is a selective reducing agent. It reduces carboxylic acids, carboxylic acid derivatives and nitriles into aldehydes. It is an electrophilic reducing agent.

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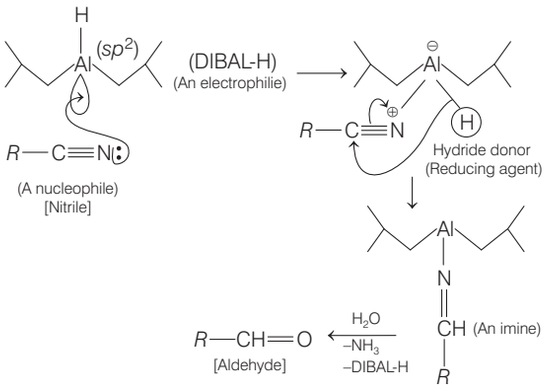
The mechanism of the reaction is as follows:



So, $R—\underset{\underset{O}{\|}}{CH}$ is the correct answer.

28 The increasing basicity order of the following compounds is

(A) $CH_3CH_2NH_2$ (B) $CH_3CH_2\underset{\underset{CH_2CH_3}{|}}{NH}$

(C) $H_3C—\underset{\underset{CH_3}{|}}{N}—CH_3$ (D) $Ph—\underset{\underset{CH_3}{|}}{N}—H$ **[2019, 9 Jan Shift-II]**

(a) (D) < (C) < (B) < (A) (b) (A) < (B) < (C) < (D)

(c) (A) < (B) < (D) < (C) (d) (D) < (C) < (A) < (B)

Ans. ***(d)***

If we consider Lewis basicity (basicity in aprotic solvents or in vapour phase), the order of basicity will be.

D < A < B < C

(2°) (1° 2° 3°)

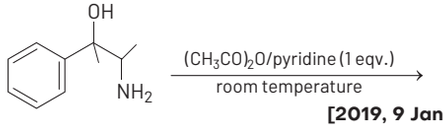
But, this order does not match with the options given. So, it has been asked on basicity of the amines in aqueous solution. When no phase is given, then basicity of amine is considered in aqueous solution as they are liquids.

In aqueous solution, basicity of 2°-amines (aliphatic) is maximum because, of the thermodynamic stability of its conjugate acid.

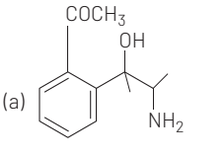
$\underset{(B)}{Et_2NH} + H_2O \rightleftharpoons \underset{\text{Conjugate acid}}{Et_2\overset{\oplus}{N}H_2} + \overset{\ominus}{O}H$

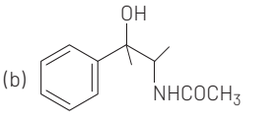
$Et_2\overset{\oplus}{N}H_2$ is a sterically symmetric tetrahedral ion as it contains equal number (two) of bulkier Et-group and small size H-atoms. Here, two H-atoms give additional stability through hydrogen bonding with H_2O (solvent) molecules.

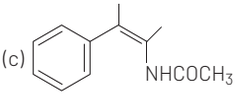
29 The major product obtained in the following reaction is

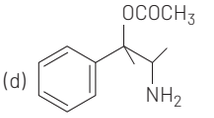


[2019, 9 Jan Shift-II]

(a) 

(b) 

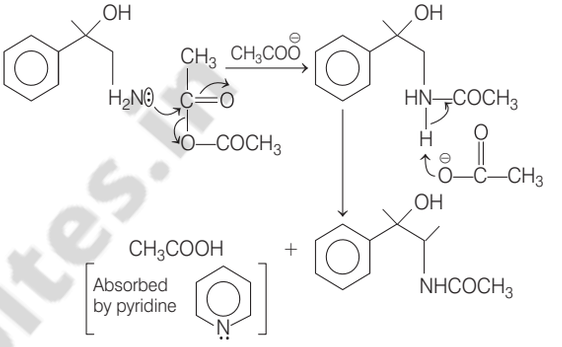
(c) 

(d) 

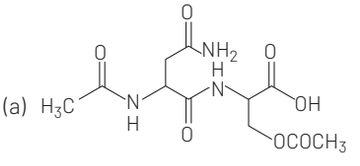
Ans. ***(b)***

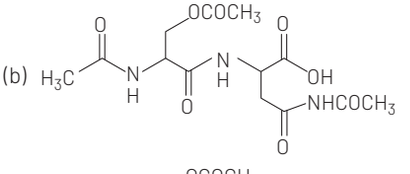
Rate of acetylation $—NH_2 > —OH$ because N-bases are stronger than O-bases. Size of N-atom is larger than O-atom and at the same time, N atom is less electronegative than O-atom.

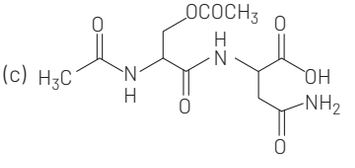
So, N-atom of the $—\ddot{N}H_2$ group can donate its lone pair of electrons (Lewis basicity) more easily than that of O atom of the $—\ddot{O}H$ group.

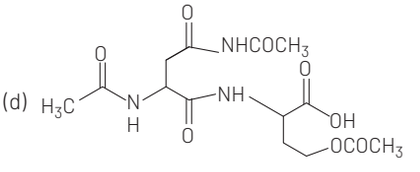


30 The correct structure of product '*P*' in the following reaction is $Asn - Ser + \underset{\text{(Excess)}}{(CH_3CO)_2O} \xrightarrow{NEt_3} P$ **[2019, 10 Jan Shift-I]**

(a) 

(b) 

(c) 

(d) 

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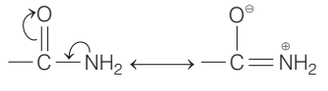
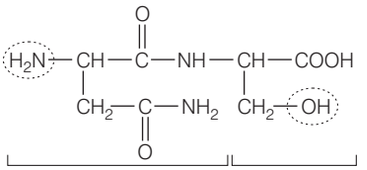
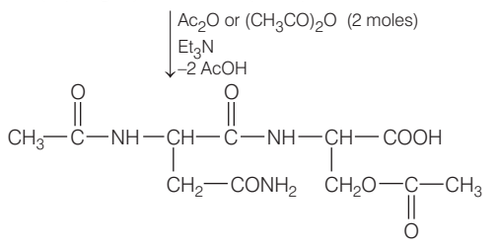
Ans. ***(a)***

Acetylation by Ac_2O / Et_3N is possible with —NH_2 (1°-amine) and —OH(alcohol) groups only, but not with '—NH_2' part of

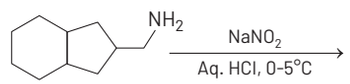
(amide) groups, because the *lp* of nitrogen in amide group is involved in resonance with $>C=O$ part.



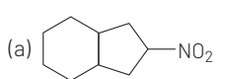


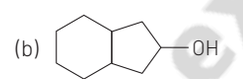


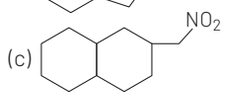
31 The major product formed in the reaction given below will be



[2019, 10 Jan Shift-I]

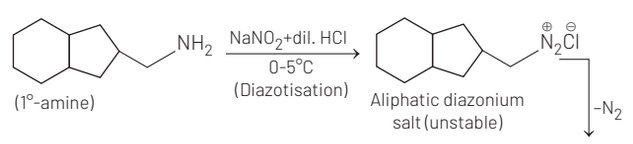


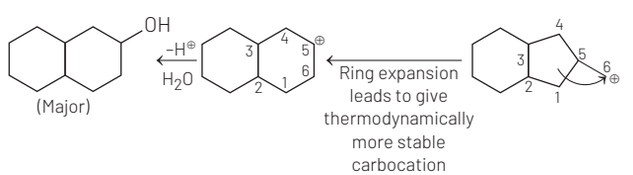




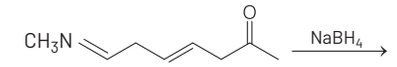
Ans. ***(*)***

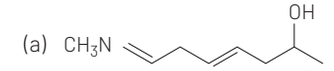
No option is the correct answer. Amines in presence of $NaNO_2$ + dil. HCl undergoes diazotisation. The diazotised product readily loses nitrogen gas with the formation of carbocation. The resulting carbocation rearranges itself to give the expanded ring.

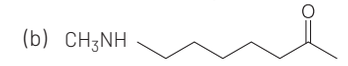


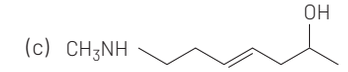


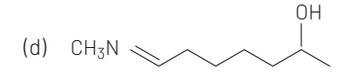
32 The major product of the following reaction is



(a) 

(b) 

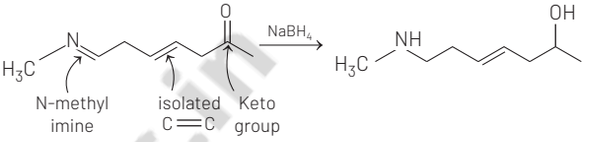
(c) 

(d) 

[2019, 10 Jan Shift-II]

Ans. ***(c)***

$NaBH_4$ is a selective reducing agent. It can reduce $>C=O$ group into alcohol, N-methyl imine group, Me—N == CH— into 2°-amine but cannot reduce an isolated C ═ C.



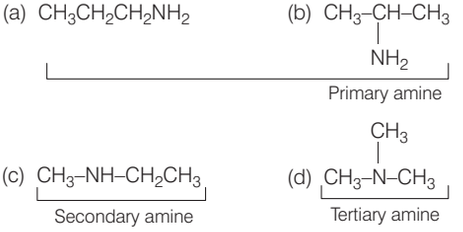
33 A compound '*X*' on treatment with Br_2 / NaOH, provided C_3H_9N, which gives positive carbylamine test. Compound '*X*' is **[2019, 11 Jan Shift-II]**

(a) $CH_3COCH_2NHCH_3$ (b) $CH_3CH_2CH_2CONH_2$

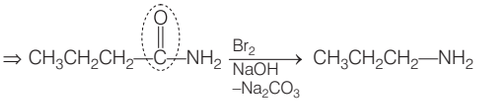
(c) $CH_3CON(CH_3)_2$ (d) $CH_3CH_2COCH_2NH_2$

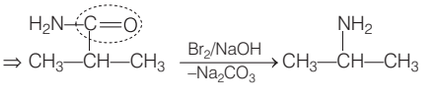
Ans. ***(b)***

The molecular formula, C_3H_9N refers to four structural isomers of amines



Here, only *a* and *b* (primary amines) can be prepared from their respective amides by Hoffmann bromamide (Br_2/NaOH) method and can give positive carbylamine test.





So, '*X*' can be $CH_3CH_2CH_2—CONH_2$ (a) or $CH_3CH(CONH_2)CH_3$ (b).

Carbylamine test given by (a) and (b)

$$CH_3CH_2CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3(CH_2)_2NC + 3KCl + 3H_2$$

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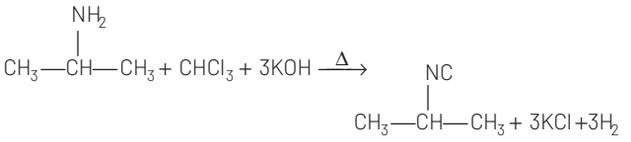
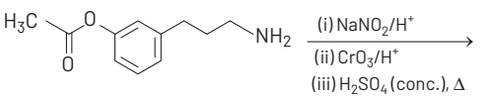
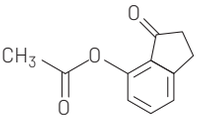


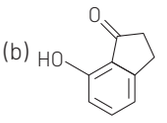
As (b) is not among the given options So, it is ruled out and compound (X) is $CH_3CH_2CH_2CONH_2$.

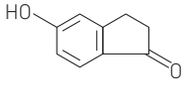
34 The major product of the following reaction is

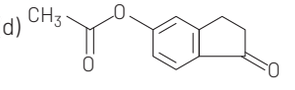


[JEE Main 2018]

(a) 

(b) 

(c) 

(d) 

Ans. ***(c)***

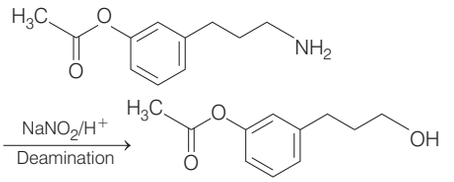
Key Idea The reaction involves:

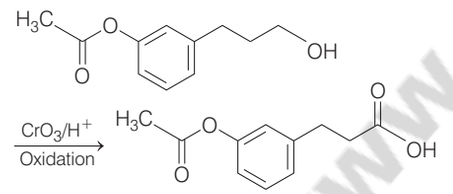
A. Deamination in step (i)

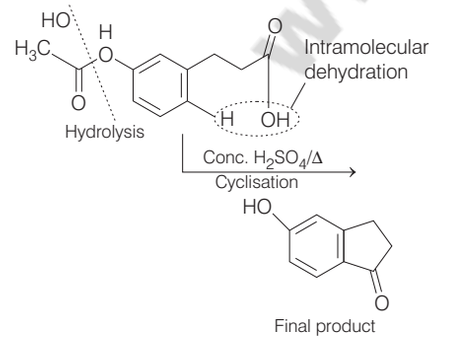
B. Oxidation in step (ii)

C. Hydroysis in step (iii)

The complete pathway of reactions is as follows:

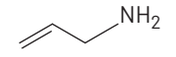
(i) 

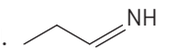
(ii) 

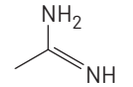
(iii) 

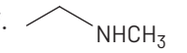
Thus, option (c) is the correct answer.

35 The increasing order of basicity of the following compounds is **[JEE Main 2018]**

I. 

II. 

III. 

IV. 

(a) (I) < (II) < (III) < (IV)

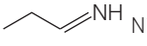
(b) (II) < (I) < (III) < (IV)

(c) (II) < (I) < (IV) < (III)

(d) (IV) < (II) < (I) < (III)

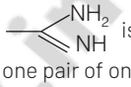
Ans. ***(d)***

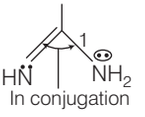
Among the given compounds the basic nature depends upon their tendency to donate electron pair.

Among the given compounds in  Nitrogen is sp^2-hybridised.

This marginally increases the electronegativity of nitrogen which in turn decreases the electron donation tendency of nitrogen.

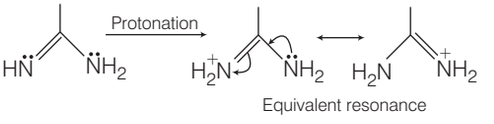
Thus making compound least basic.

Among the rest  is totally different from others as in this compound lone pair of one nitrogen are in conjugation with π bond i.e.

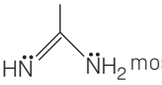


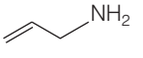
In conjugation

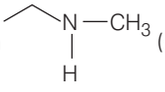
As a result of this conjugation the cation formed after protonation becomes resonance stabilised



Equivalent resonance

This equivalent resonance in cation makes  most basic among all.

Categorisation is very simple between rest two as 

(primary amine) is less basic than  (secondary amine)

Hence, the correct order is

(II) < (I) < (IV) < (III)

i.e. option (c) is correct.

36 In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are **[JEE Main 2016]**

(a) four moles of NaOH and two moles of Br_2

(b) two moles of NaOH and two moles of Br_2

(c) four moles of NaOH and one mole of Br_2

(d) one mole of NaOH and one mole of Br_2

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Ans. *(c)*

Hofmann-bromamide degradation reaction is given as:

$$R\text{CONH}_2 + 4\text{NaOH} + \text{Br}_2 \longrightarrow \underset{(1^\circ \text{ amine})}{\text{RNH}_2} + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$$

Hence, four moles of NaOH and one mole of Br_2 are used.

37 On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is **[JEE Main 2014]**

(a) an alkanol
(b) an alkanediol
(c) an alkyl cyanide
(d) an alkyl isocyanide

Ans. *(d)*

Reaction of aliphatic primary amine with chloroform and ethanolic potassium hydroxide, leads to the formation of isocyanides/carbylamines. Thus, this reaction is called carbylamine reaction.

$$R\text{—NH}_2 + \text{CHCl}_3 + \text{KOH} \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{\text{R—NC}} + 3\text{KCl} + 3\text{H}_2\text{O}$$

38 Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[JEE Main 2014]**

(a) $(CH_3)_2NH$ (b) CH_3NH_2
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

Ans. *(a)*

It is known that, $pK_b = -\log k_b$

Thus, larger the value of k_b, smaller is the value of pK_b and hence, stronger is the base.

The order of basic strength of amines is as follows

$$(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N} > C_6H_5\ddot{N}H_2$$

The basic strength of amines depends on the inductive effect as will as steric hinderance of alkyl groups. Hence, $(CH_3)_2\ddot{N}H$ [secondary amine] possess the smallest value of pK_b.

39 An organic compound *A* on reacting with NH_3 gives *B*. On heating *B* gives *C*. *C* in the presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. *A* is **[JEE Main 2013]**

(a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$ (b) $CH_3CH_2CH_2CH_2COOH$
(c) CH_3CH_2COOH (d) CH_3COOH

Ans. *(c)*

$$A \xrightarrow{NH_3} B \xrightarrow{\Delta} C \xrightarrow{KOH/Br_2} CH_3CH_2NH_2$$

The reaction of C with KOH/Br_2 to give amine is called Hofmann bromamide reaction. This reaction is give by acid amides only in which

$R-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2$ group undergoes rearrangement along with the loss of CO_2 molecule. Thus, the compound C must be acid amide with three carbon atoms. Hence, the compound C is

$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2$.

Since, all the options shows that *A* is an acid and it forms acid amide on reaction with NH_3. Thus, acid must contain three carbon atoms. Hence, the compound *A* is CH_3CH_2COOH. The complete series of reaction can be represented as

$$\underset{(A)}{CH_3CH_2COOH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2COO^- NH_4^+} \xrightarrow{\Delta} CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{bromamide reaction}]{\text{Hofmann}} \underset{(C)}{} \xrightarrow{KOH/Br_2} CH_3CH_2NH_2$$

40 A compound with molecular mass 180 μ is acylated with CH_3COCl, to get a compound with molecular mass 390 μ. The number of amino groups present per molecule of the former compound is **[JEE Main 2013]**

(a) 6 (b) 2 (c) 5 (d) 4

Ans. *(c)*

During acetylation, one H atom with atomic mass 1 amu of $-NH_2$ group is replaced by an acetyl group CH_3CO [molecular mass = 434 μ]. Thus,

$$-NH_2 + CH_3COCl \longrightarrow -NHCOCH_3 + HCl$$

The above equation suggests that, the acylation of each $-NH_2$ group increases the mass by 42 μ [43 – 1]. If the molecular mass of the organic compound is 180 μ while that of the acylated product is 390 μ, then the increase in the mass due to acylation is given by

$$390 - 180 = 210\,\mu$$

Hence, the number of $-NH_2$ groups $= \dfrac{210\,\mu}{42\,\mu} = 5$

41 Which one of the following is the strongest base in aqueous solution ? **[AIEEE 2007]**

(a) Trimethylamine (b) Aniline
(c) Dimethylamine (d) Methylamine

Ans. *(c)*

In aqueous solution, basicity order is

$$\underset{2^\circ}{\text{Dimethylamine}} > \underset{1^\circ}{\text{methylamine}} > \underset{3^\circ}{\text{trimethylamine}} > \text{aniline}$$

This order depends upon the inductive effect and steric hinderance of alkyl groups.

42 In the chemical reaction,

$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow (A) + (B) + 3H_2O$,

the compounds (*A*) and (*B*) are respectively **[AIEEE 2007]**

(a) C_2H_5CN and 3KCl
(b) $CH_3CH_2CONH_2$ and 3KCl
(c) C_2H_5NC and 3KCl
(d) C_2H_5NC and 3KCl

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Ans. *(c)*

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow[(alc)]{} \underset{(A)}{CH_3CH_2{-}N} \rightleftharpoons \underset{(B)}{C} + 3KCl + 3H_2O$$

The above reaction is called carbylamine reaction in which isocyanides or carbylamines are produced.

43 Which one of the following methods is neither meant for the synthesis nor for separation of amines ? **[AIEEE 2005]**

(a) Curtius reaction (b) Wurtz reaction
(c) Hofmann method (d) Hinsberg method

Ans. *(b)*

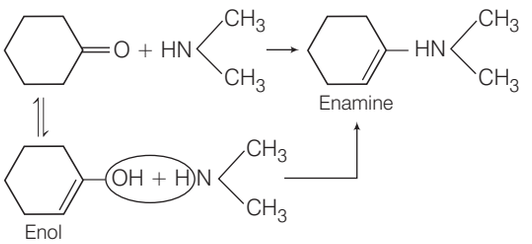
Wurtz reaction is used to prepare alkanes from alkyl halides.

$$2R{-}X + 2Na \xrightarrow{\text{Dry ether}} R{-}R + 2NaX$$

44 Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound. Water during the reaction is continuously removed. The compound formed is generally known as

(a) an amine (b) an imine **[AIEEE 2005]**
(c) an enamine (d) a Schiff 's base

Ans. *(c)*



45 An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating, it gives NH_3 alongwith a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is

(a) $CH_3CH_2CONH_2$ (b) $(NH_2)_2CO$ **[AIEEE 2005]**
(c) CH_3CONH_2 (d) CH_3NCO

Ans. *(b)*

Element	Percentage	$\frac{\text{Percentage}}{\text{at. wt.}}$	Simple Ratio
C	20.0	$\frac{20.0}{12} = 1.66$	$\frac{1.66}{1.66} = 1$
H	6.67	$\frac{6.67}{1} = 6.67$	$\frac{6.67}{1.66} = 4$
N	46.67	$\frac{46.67}{14} = 3.33$	$\frac{3.33}{1.66} = 2$
O	26.66	$\frac{26.66}{16} = 1.66$	$\frac{1.66}{1.66} = 1$

Empirical formula = CH_4N_2O

Empirical formula weight = $12 + (4 \times 1) + (2 \times 14) + 16 = 60$

$$\therefore \quad n = \frac{\text{Mole formula weight}}{\text{Emp formula weight}} = \frac{60}{60} = 1$$

∴ Molecular formula = CH_4N_2O

Given compound gives biuret test, thus given compound is urea $(NH_2)_2CO$.

$$NH_2CONH_2 + HNHCONH_2 \xrightarrow{\Delta} \underset{\text{Biuret}}{NH_2CONHCONH_2} + NH_3$$

$$\text{Biuret} \xrightarrow{\text{as } CuSO_4} \text{Violet colour}$$

46 The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[AIEEE 2003]**

(a) $CH_3NH_2 < NH_3 < (CH_3)_2NH$ (b) $(CH_3)_2NH < NH_3 < CH_3NH_2$
(c) $NH_3 < CH_3NH_2 < (CH_3)_2NH$ (d) $CH_3NH_2 < (CH_3)_2NH < NH_3$

Ans. *(c)*

The basicity of an amine in aqueous solution primarily depends upon the stability of the ammonium cation or the conjugate acid formed by accepting the proton from water.

$$RNH_2 + H_2O \rightleftharpoons \underset{\text{[ammonium cation]}}{R\overset{+}{N}H_3} + OH^-$$

The stability of the ammonium cation depends upon

(i) + *I* effect of alkyl groups
(ii) Extent of H-bonding with water molecules
(iii) Steric effects of the alkyl groups

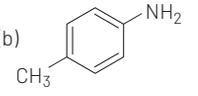
On the basis of above factors, the basic strength of amine is as follows

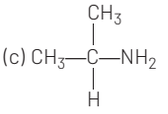
$$(CH_3)_2NH > CH_3NH_2 > NH_3$$

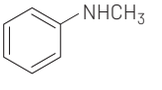
(+*I* effect of $-CH_3$ group predominates)

TOPIC 2
Aromatic Amines

47 Which one of the following gives the most stable diazonium salt ? **[2021, 01 Sep Shift-II]**

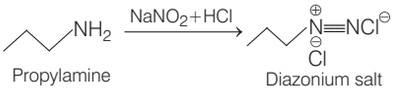
(a) $CH_3{-}CH_2{-}CH_2{-}NH_2$ (b) 

(c) 

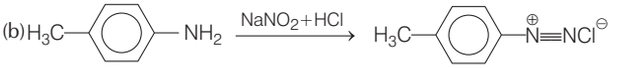
(d) 

Ans. *(b)*

Primary amines react with $NaNO_2$ and HCl to give diazonium salts.

(a) 

Propylamine Diazonium salt

(b) 

p-methylaniline Most stable diazonium salt due to +H effect

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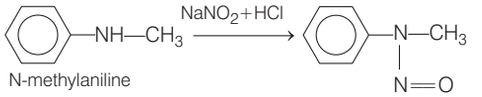
(c) $CH_3-CH(CH_3)-NH_2 \xrightarrow{NaNO_2+HCl} H_3C-CH(CH_3)-\overset{\oplus}{N}\equiv N$

2-methylethanamine

(d) 

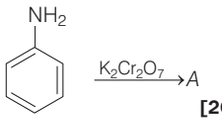
N-methylaniline

N-alkyl nitroso amine

Diazonium salt is not formed rather N-alkylnitroso amine is formed as product.

∴ In option (b) the most stable diazonium salt is formed.

48 Identify *A* in the following reaction.

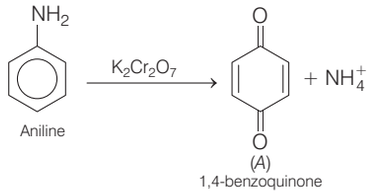


[2021, 01 Sep Shift-II]

Ans. ***(a)***

Aniline reacts with potassium dichromate ($K_2Cr_2O_7$) to form 1,4-benzoquinone as the product. The nascent oxygen produced from $K_2Cr_2O_7$ reacts with aniline to form 1,4-benzoquinone with the removal of NH_4^+ ion.

This reaction involves oxidation of aniline.

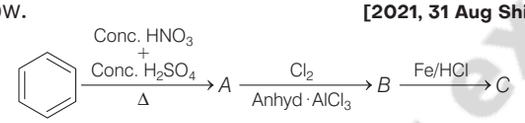


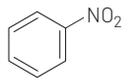
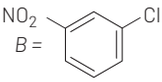
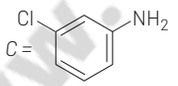
Aniline

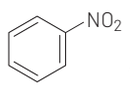
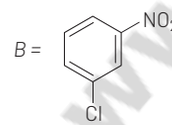
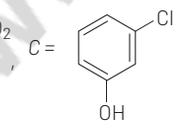
(*A*)
1,4-benzoquinone

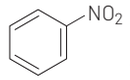
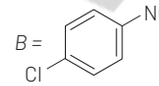
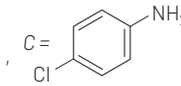
49 Identify correct *A*, *B* and *C* in the reaction sequence given below.

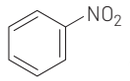
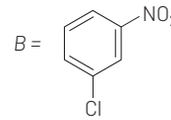
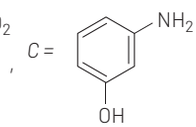
[2021, 31 Aug Shift-II]



(a) *A* =  , *B* =  , *C* = 

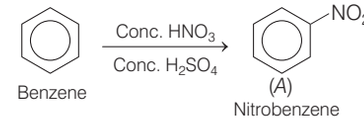
(b) *A* =  , *B* =  , *C* = 

(c) *A* =  , *B* =  , *C* = 

(d) *A* =  , *B* =  , *C* = 

Ans. ***(a)***

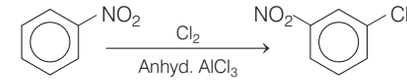
Benzene undergoes nitration on reaction with conc. HNO_3 and conc. H_2SO_4.



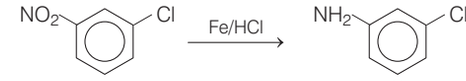
Benzene

(*A*)
Nitrobenzene

Nitrobenzene on reaction with Cl_2/ anhyd. $AlCl_3$ undergoes electrophilic substitution reaction to give 1-chloro-3-nitro benzene, which on reaction with Fe/HCl gives chloroaniline.



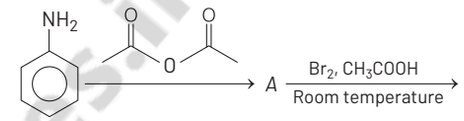
(*B*)
1-chloro-3-nitro benzene

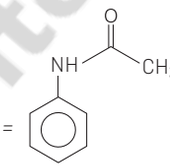
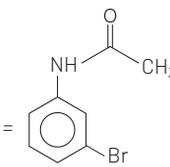


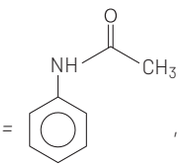
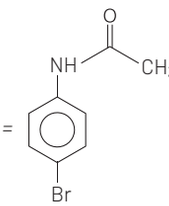
(*C*)
Chloroaniline

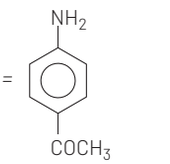
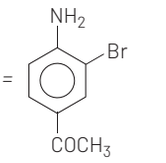
50 The major products *A* and *B* formed in the following reaction sequence are

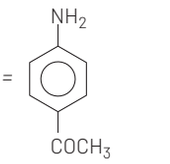
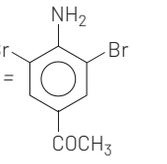
[2021, 31 Aug Shift-II]



(a) *A* =  , *B* = 

(b) *A* =  , *B* = 

(c) *A* =  , *B* = 

(d) *A* =  , *B* = 

Ans. ***(b)***

Aniline reacts with acetic anhydride to give acetanilide.

The acetic acid part is removed and N-acylation takes place by nucleophilic substitution reaction.

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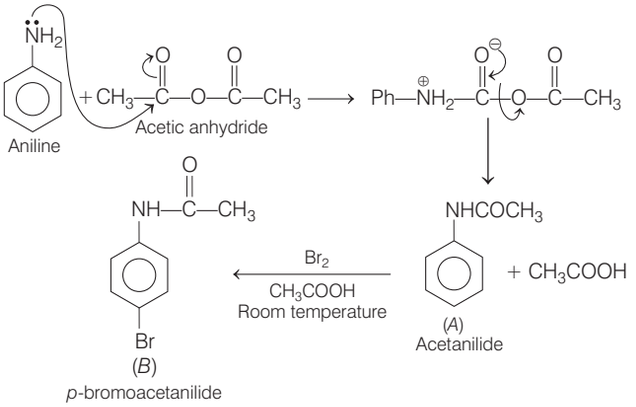


Acetanilide is brominated with bromine/acetic acid. As —$NHCOCH_3$ is *ortho/para* directing group (since lone pair on N activates the ring).

Bromine attached to *para* position is the major product losse.

51 The total number of reagents from those given below, that can convert nitrobenzene into aniline is ..... (Integer answer) **[2021, 31 Aug Shift-I]**

I. Sn – HCl II. Sn – NH_4OH

III. Fe – HCl IV. Zn – HCl

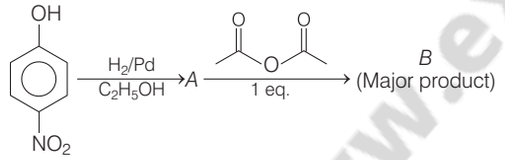
V. H_2 – Pd VI. H_2-Raney nickel

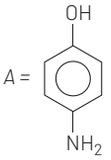
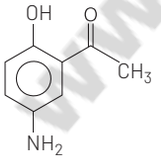
Ans. ***(5)***

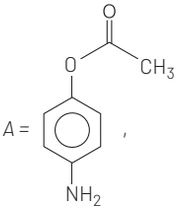
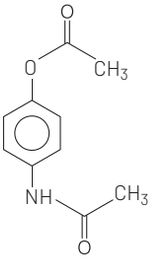
The nitrobenzene can be reduced to aniline *via* following reagents.

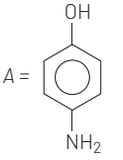
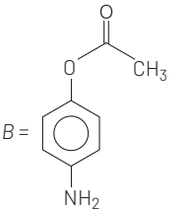
(I) Sn-HCl (V) H_2-Pd (III) Fe-HCl (VI) H_2 (Raney Ni) (IV) Zn-HCl

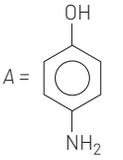
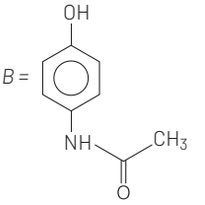
52 The correct structures of *A* and *B* formed in the following reactions are **[2021, 27 Aug Shift-II]**



(a) *A* =  , *B* = 

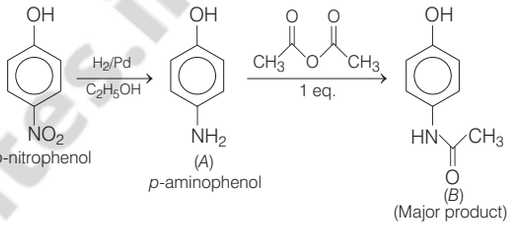
(b) *A* =  , *B* = 

(c) *A* =  , *B* = 

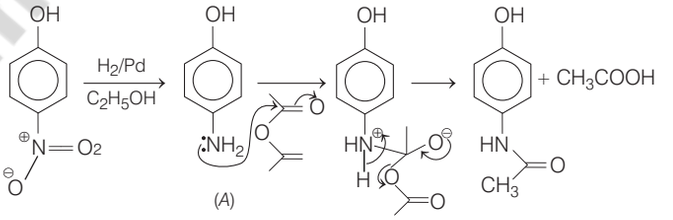
(d) *A* =  , *B* = 

Ans. ***(d)***

Since, only one equivalent of acetic anhydride is present and — NH_2 group is more nucleophilic than —OH group due to lower electronegativity of nitrogen. So, it attacks at the carbonyl center of acetic anhydride forming the product *B*.



Mechanism



Therefore, the option (d) is correct.

53 Given below are two statements.

Statement I Aniline is less basic than acetamide.

Statement II In aniline, the lone pair of electrons on nitrogen atom is delocalised over benzene ring due to resonance and hence less available to a proton.

Choose the most appropriate option : **[2021, 27 July Shift-I]**

(a) Statement I is true but statement II is false.

(b) Statement I is false but statement II is true.

(c) Both statement I and statement II are true.

(d) Both statement I and statement II are false.

Ans. ***(b)***

Statement I is false but Statement II is true.

Aniline ($C_6H_5NH_2$) is more basic than acetamide (C_2H_5NO) because in acetamide lone pair of electron present on nitrogen is delocalised to more electronegative element, i.e. oxygen.

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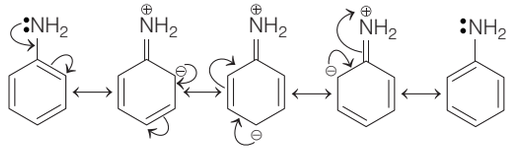
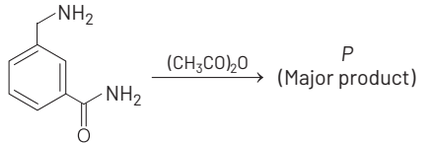
As lone pair of N in acetamide is in conjugation with C═O that is strong electron withdrawing than phenyl group, so lone pair of N is unavailable for proton, so it is less basic than aniline.

In aniline, lone pair of electrons on the N atom is delocalised over benzene ring.



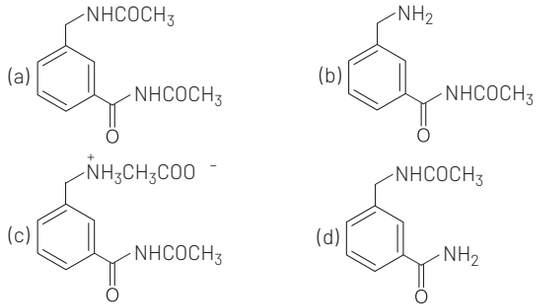
Ph — NH_2 > *R*$CONH_2$ (Basic strength).

54



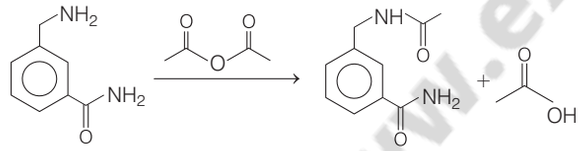
The major product in the above reaction is

[2021, 26 Aug Shift-II]



Ans. ***(d)***

Since — CH_2 — NH_2 is more basic, the resulting amide will fail to react further. Therefore, imide formation takes place at only one site (i.e. primary amine). The complete reaction is as follows :



55 Given below are two statements, one is labelled as : Assertion (A) and other is labelled as Reason (R).

Assertion (A) Gabriel phthalimide synthesis cannot be used to prepare aromatic primary amines.

Reason (R) Aryl halides do not undergo nucleophilic substitution reaction.

In the light of the above statements, choose the correct answer from the options given below

[2021, 22 July Shift-I]

(a) Both (A) and (R) true but (R) is not the correct explanation of (A).
(b) (A) is false but (R) is true.
(c) Both (A) and (R) true and (R) is correct explanation of (A).
(d) (A) is true but (R) is false.

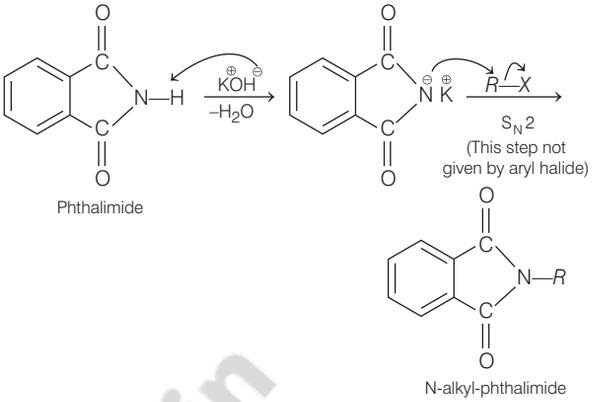
Ans. ***(c)***

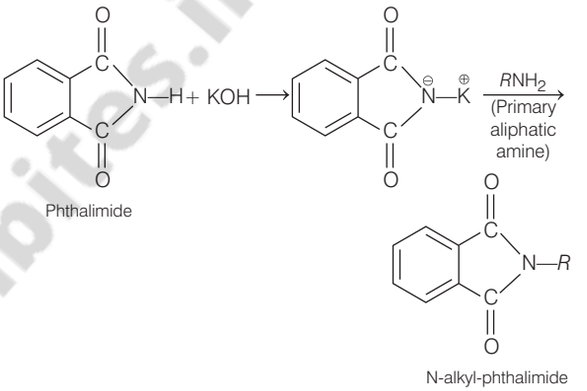
Both (A) and (R) are true and (R) is correct explanation of (A).

Aromatic halide does not give S_N2 reaction.

Gabriel pthalimide synthesis is used to form primary aliphatic amine, because aryl halides do not undergo nucleophilic substitution reaction.

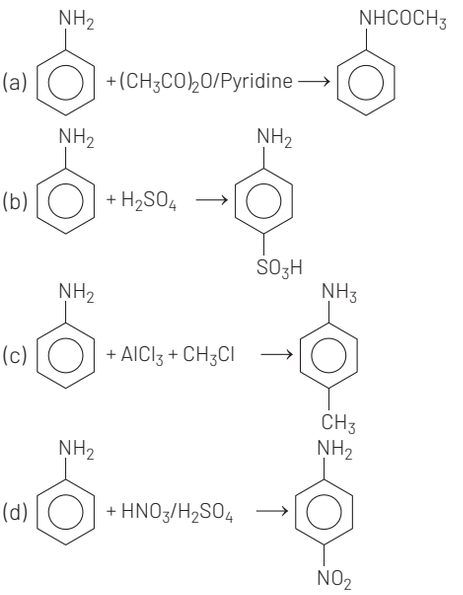
Gabriel phthalimide reaction





56 Which one of the following reactions does not occur?

[2021, 22 July Shift-II]



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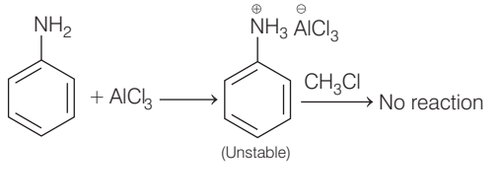
Ans. ***(c)***

Friedel-Craft reaction is not possible in highly activated ring, i.e. aniline because NH_2 group forms complex with Lewis acid and deactivate the ring.

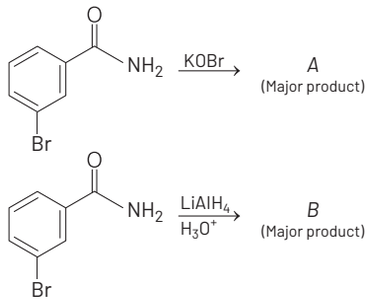
Chemical reaction is as follows :



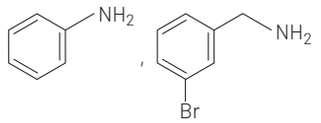
Due to lone pair of electrons on N, aniline is a strong Lewis base. So, an acid base reaction occur between aniline and $AlCl_3$ leading to anilinium salt formation.

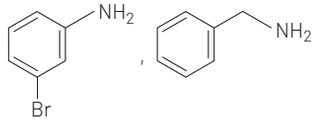
Since, $\overset{+}{N}H_3$ is a deactivating group and hence electrophilic substitution *via* Friedel-Craft alkylation does take place.

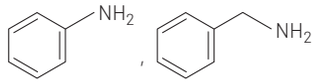
57

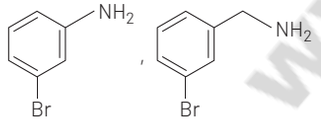


In the above reactions, products *A* and *B* respectively are **[2021, 20 July Shift-II]**

(a) 

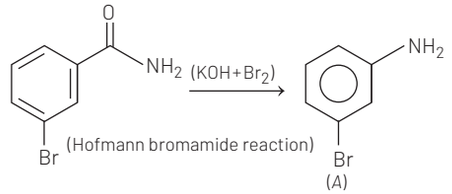
(b) 

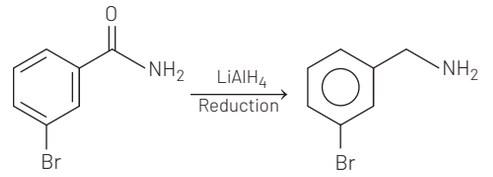
(c) 

(d) 

Ans. ***(d)***

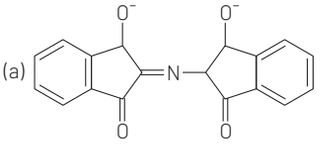
Hofmann reagent reduces amide to amine with one carbon less. This reaction is known as Hofmann bromamide reaction.

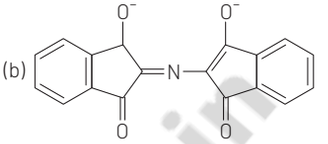


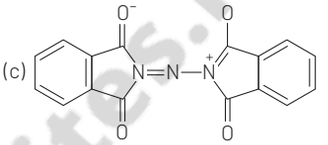


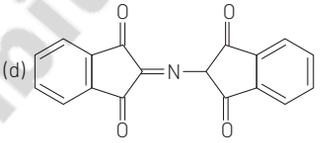
$LiAlH_4$ reduces amide to primary amine with same number of carbon atom.

58 The correct structure of Rhumann's Purple, the compound formed in the reaction of ninhydrin with proteins is **[2021, 20 July Shift-I]**

(a) 

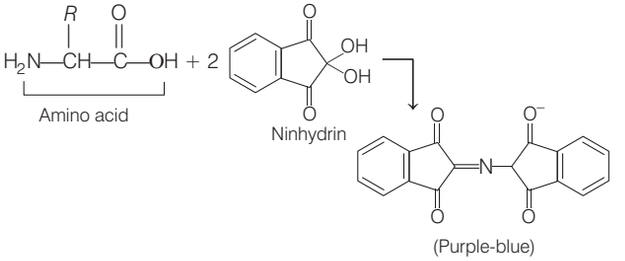
(b) 

(c) 

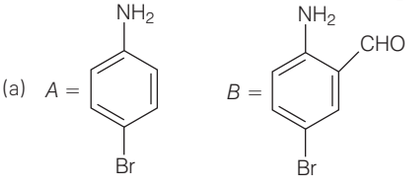
(d) 

Ans. ***(d)***

Rhumann's purple is confirmatory test for the presence of protein. The correct structure of Rhumann's Purple, the compound formed in the reaction of ninhydrin with proteins is an follows



59 Hofmann bromamide degradation of benzamide gives product *A*, which upon heating with $CHCl_3$ and NaOH gives product *B*. The structures of *A* and *B* are **[2021, 17 March Shift-I]**

(a) 

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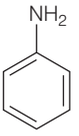
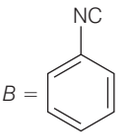
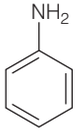
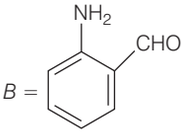
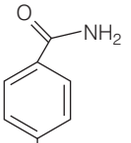
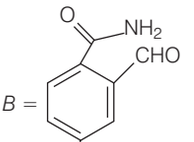
(b) *A* =  *B* = 

(c) *A* =  *B* = 

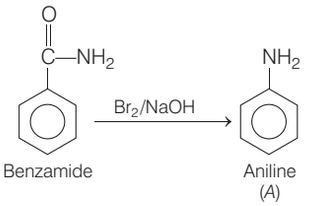
(d) *A* =  *B* = 

Ans. ***(b)***

Hofmann bromamide degradation of benzamide gives product aniline (*A*), which upon heating with $CHCl_3$ and NaOH gives product benzene isocyanide (*B*), by carbylamine reaction.

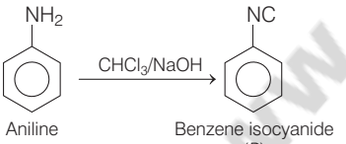
Hofmann bromamide degradation method is for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.

The amine formed contains one carbon less than that present in the amide.



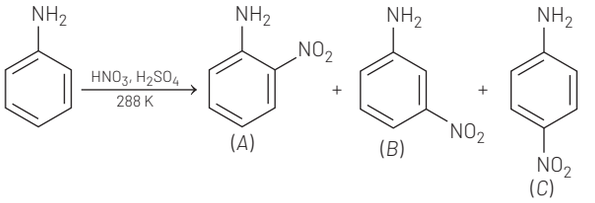
Hofmann bromamide reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.



Carbylamine reaction

Note Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

60 

Consider the given reaction, percentage yield of

[2021, 18 March Shift-II]

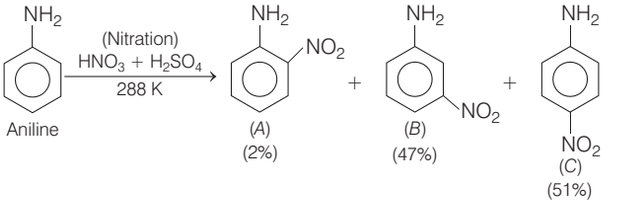
(a) (*C*) > (*A*) > (*B*) (b) (*B*) > (*C*) > (*A*)

(c) (*A*) > (*C*) > (*B*) (d) (*C*) > (*B*) > (*A*)

Ans. ***(d)***

During nitration of aniline, *meta*-nitroaniline is also formed as product due to formation of NH_3^+ group which is meta directing group under strongly acidic medium. The percentage of *p*, *m* and *o* product is 51%, 47% and 2%, respectively.

Reaction is as follows



% yield order is *C* > *B* > *A*.

61 A. phenyl methanamine B. N,N-dimethylaniline

C. N-methyl aniline D. Benzenamine

Choose the correct order of basic nature of the above amines. **[2021, 26 Feb Shift-II]**

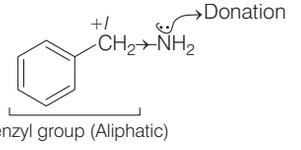
(a) A > C > B > D (b) D > C > B > A

(c) D > B > C > A (d) A > B > C > D

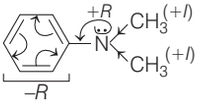
Ans. ***(d)***

In phenyl methanamine, the lone pair on nitrogen of $—NH_2$ group is localised and does not undergoes resonance as attached to sp^3-hybridised C-atom.

Phenyl methanamine or benzyl amine

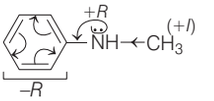


(*B*), (*C*) and (*D*) are aromatic amines in which lone pair of electrons of N-atoms goes in resonance (+*R* effect) with the benzene ring. So, Lewis basicity or donation of lone of electrons of these amines will be decreased in comparison to (*A*).

(B) 

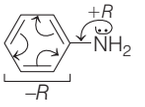
N, N-dimethyl aniline (3°-amine)

+ *I* effects of two $—CH_3$ groups are in compensation with –*R*-effect of the ring.

(C) 

N-methyl aniline (2°-amine)

+ *I* effect of one $—CH_3$ group is trying to compensate – *R* effect of the ring.

(D) 

Benzenamine or aniline (1° amine)

It has no + *I*-effect on N-atom to outweigh –*R*-effect of the ring.

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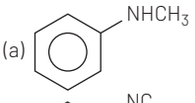
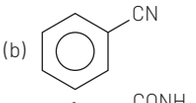
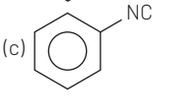
So, *A* is purely aliphatic 1°-amine. *B* is aromatic 3°-amine with more aliphatic nature (for two —CH_3 groups). *C* is aromatic 2°-amine with less aliphatic nature (for one —CH_3 group). *D* is purely aromatic 1°-amine.

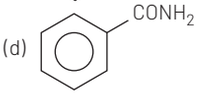
Hence basicity order is $A > B > C > D$.

62 Carbylamine test is used to detect the presence of primary amino group in an organic compound. Which of the following compound is formed when this test is performed with aniline? **[2021, 25 Feb Shift-II]**

(a) 

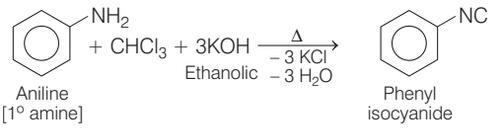
(b) 

(c) 

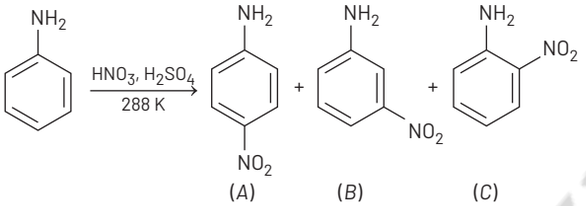
(d) 

Ans. ***(c)***

Aniline on carbylamine reaction produces a foul smelling gas, phenyl isocyanide (C_6H_5NC).



Carbylamine test is used to detect aliphatic and aromatic primary amines.

63 

Correct statement about the given chemical reaction is **[2021, 25 Feb Shift-II]**

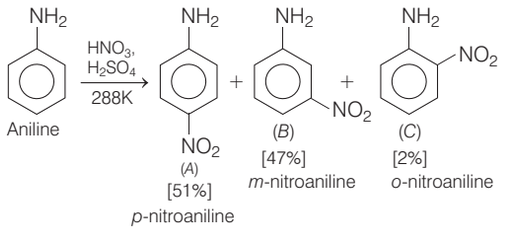
(a) —$\ddot{N}H_2$ group is *ortho* and *para* directing, so product (*B*) is not possible.

(b) reaction is possible and compound (*B*) will be the major product.

(c) the reaction will form sulphonated product instead of nitration.

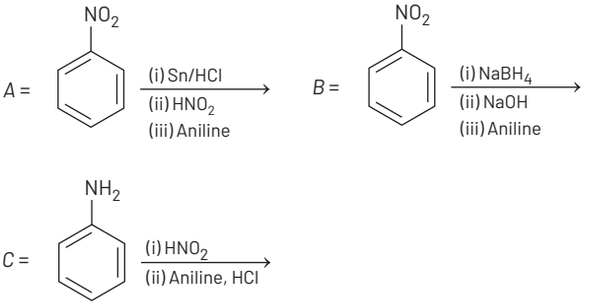
(d) reaction is possible and compound (*A*) will be major product.

Ans. ***(d)***



During nitration, in strongly acidic medium, aniline gets protonated to form the anilinium ion i.e, (C_6H_5 —$\overset{\oplus}{N}H_3$) which is *meta*-directing as —$\overset{\oplus}{N}H_3$ is an electron withdrawing (–*I*) group. As a result, we get *meta*-nitro aniline (*B*) as the major product.

64 Which of the following reaction(s) will not give *p*-aminoazobenzene? **[2021, 25 Feb Shift-I]**

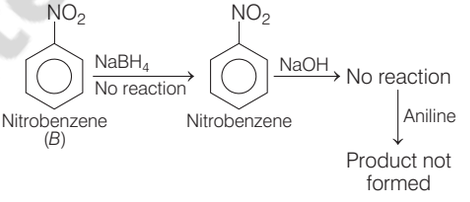


(a) *A* only (b) *C* only

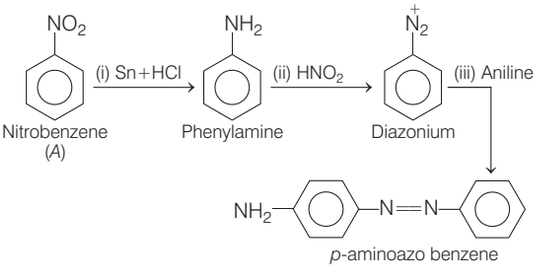
(c) *B* only (d) *A* and *B*

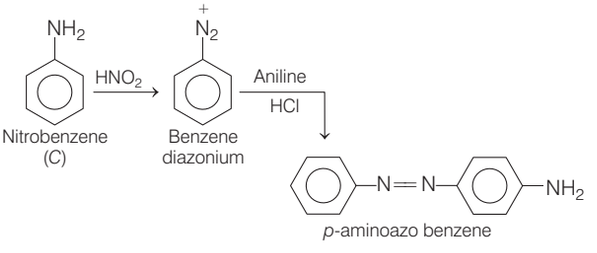
Ans. ***(c)***

Nitrobenzene in presence of $NaBH_4$, NaOH and aniline will not give *p*-amino azobenzene.



In case of (*A*) and (*C*), coupling reaction takes place as the medium is quite acidic follows





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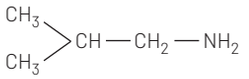
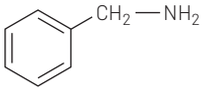
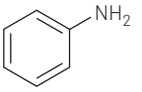
65 The total number of amines among the following which can be synthesised by Gabriel synthesis is ..... .

[2021, 24 Feb Shift-II]

(a) 
(b) $CH_3CH_2NH_2$

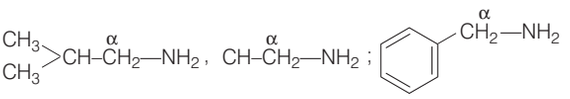
(c) 
(d) 

Ans. ***(3)***

Gabriel phthalimide synthesis is used to prepare 1° aliphatic or alicyclic amine. Hence, amine which can be synthesised by Gabriel phthalimide synthesis method contains α-carbon.

Aniline ($C_6H_5NH_2$) does not contain α -C cannot be prepared by Gabriel reaction.

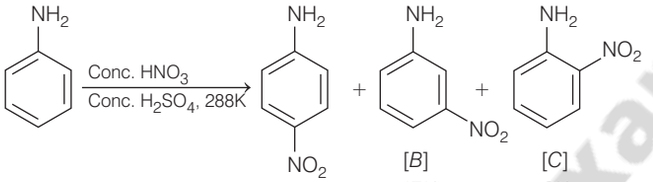
Rest amines all contain α-C in its respective position, hence they can easily give Gabriel phthalimide reaction.



∴ Three amins out of given four anions can be prepared by Gabriel synthesis.

66 In the following reaction the reason why *meta*-nitro product also formed is

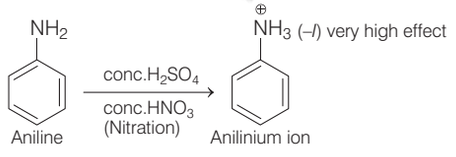
[2021, 24 Feb Shift-I]



(a) $-NH_2$ group is highly *meta*-directive
(b) $-NO_2$ substitution always takes place at *meta*-position
(c) Formation of anilinium ion
(d) Low temperature

Ans. ***(c)***

Aniline on protonation forms anilinium ion, which is *meta*-directing. So, a considerable amount of *meta* product is formed alongwith *o*-nitroaniline and *p*-nitroaniline.

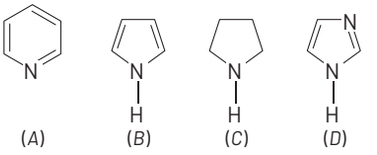


Nitrating mixture is mixture of conc. HNO_3 and a conc. H_2SO_4. When aniline is reacted with nitrating mixture *ortho*, *meta* and *para* nitroanilines are obtained.

Aniline being basic in nature, reacts with acids to form anilinium ion which is *meta* directing.

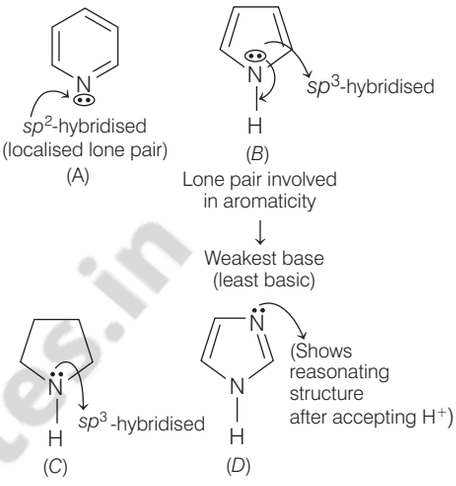
67 The increasing order of basicity of the following compounds is

[2020, 5 Sep Shift-I]

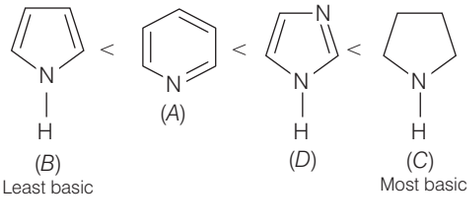


(a) (*A*) < (*B*) < (*C*) < (*D*)
(b) (*D*) < (*A*) < (*B*) < (*C*)
(c) (*B*) < (*A*) < (*D*) < (*C*)
(d) (*B*) < (*A*) < (*C*) < (*D*)

Ans. ***(c)***



More free lone pair of electron for donation, hence most basic.

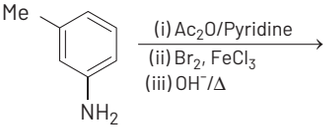


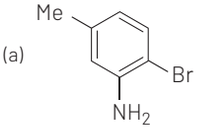
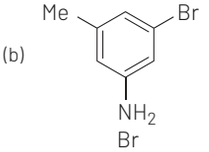
Hence, correct increasing order of basicity is

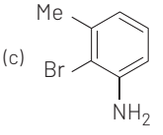
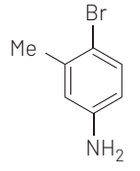
(*B*) < (*A*) < (*D*) < (*C*)

68 The final major product of the following reaction is

[2020, 5 Sep Shift-II]



(a) 
(b) 

(c) 
(d) 

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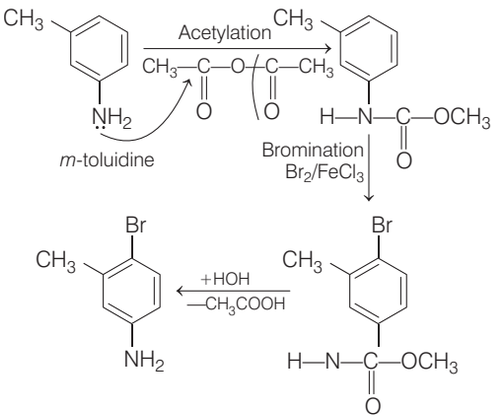
Ans. ***(d)***



The basic nature of *m*-toluidine is not greatly affected by the $—CH_3$ group.

$—NH—\overset{\overset{O}{\|}}{C}—OCH_3$ is moderately activating

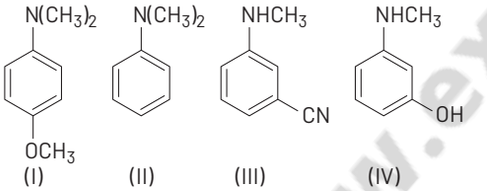
group, its activating nature overcome weak activating $—CH_3$ group.

Due to bulky nature of $—NH\overset{\overset{O}{\|}}{C}—CH_3$ attack

happen *para* to $—NHCO-CH_3$.

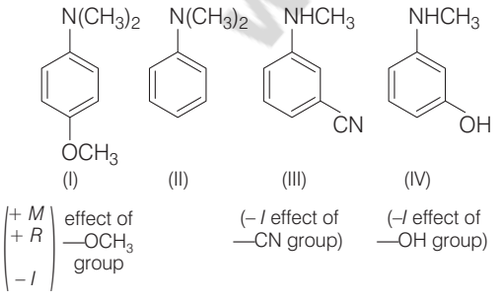
Here, NH_2 group has been protected by forming its aceyl derivative and as such if does not interfere in the bromination.

69 The increasing order of pK_b values of the following compounds is **[2020, 6 Sep Shift-I]**



(a) II < IV < III < I (b) I < II < IV < III
(c) II < I < III < IV (d) I < II < III < IV

Ans. ***(b)***



pK_b is inversely proportional to basic strength and as the electron density increases in the ring, K_b will increases and pK_a pK_a value decreases. Electron density within the ring is maximum in (I) thus it has least pK_b value. So, option (a), (c) and (d) are incorrect.

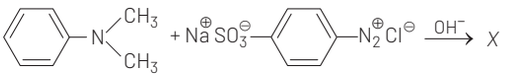
In (III) structure, —CN group attached at *meta*-position, thus electron density is less affected, so pK_b value is more than structure (IV).

Thus decreasing order for K_b is (I) > (II) > (IV) > (III)

∴ Order of pK_b : (III) > (IV) > (II) > (I).

Hence, the correct option is (b).

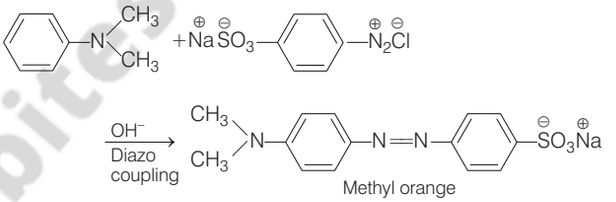
70 Consider the following reaction :



The product '*X*' is used **[2020, 7 Jan Shift-I]**

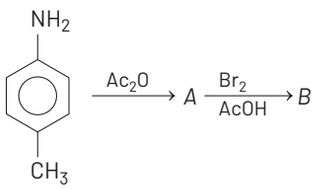
(a) in acid base titration as an indicator
(b) in protein estimation as an alternative to ninhydrin
(c) as food grade colourant
(d) in laboratory test for phenols

Ans. ***(a)***

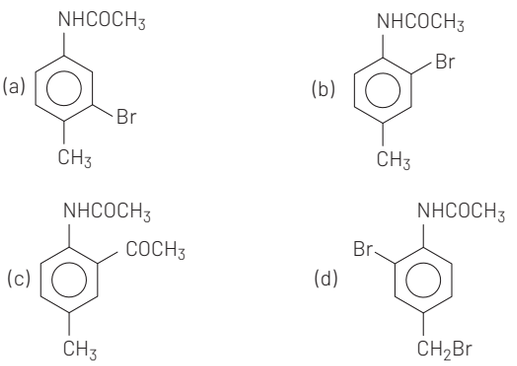


Methyl orange is used as an indicator in acid-base titration.

71 In the following reaction sequence,



the major product *B* is: **[2020, 7 Jan Shift-II]**



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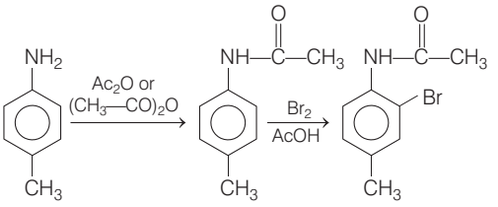
Ans. ***(b)***

The first step of the reaction is acylation.

In the second step of reaction, $-\ddot{N}H-\overset{O}{\overset{\|}{C}}-CH_3$ has $+R$ (or $+M$) effect, so it acts as *ortho/para*-directing group. But, since *para* position has CH_3 group, substitution at *ortho* takes place. $-CH_3$ has weak *ortho-/para-* directing effect due to hyperconjugation, but it is suppressed due to more predominant effect of $-\ddot{N}H-\overset{O}{\overset{\|}{C}}-CH_3$.

Thus, the complete reaction is given as follows :



72 Kjeldahl's method cannot be used to estimate nitrogen for which of the following compounds?

[2020, 8 Jan Shift-II]

(a) $C_6H_5NO_2$ (b) $NH_2-\overset{O}{\overset{\|}{C}}-NH_2$

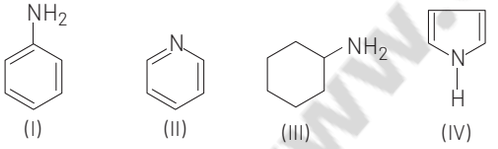
(c) $CH_3CH_2-C\equiv N$ (d) $C_6H_5NH_2$

Ans. ***(a)***

Kjeldahl's method cannot be used for nitro compounds, diazo compounds and compounds with nitrogen in a ring, because these on reaction with H_2SO_4 do not give ammonium ion.

73 The decreasing order of basicity of the following amines is

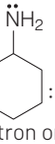
[2020, 9 Jan Shift-II]



(a) (III) > (I) > (II) > (IV)
(b) (III) > (II) > (I) > (IV)
(c) (I) > (III) > (IV) > (II)
(d) (II) > (III) > (IV) > (I)

Ans. ***(b)***

Among the given options, compound (III) has maximum basicity.



III. : No resonance or delocalisation of lone pair of electron on nitrogen.

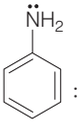
The ring contains sp^3 carbon atoms that cause $+I$-effect.

∴ More basic among options.

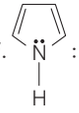
II. : No resonance or delocalisation of lone pair of electrons on nitrogen.

The ring contains sp^2 carbon atoms that have $-I$-effect, compared to sp^3 C-atoms.

∴ Less basic than compound III.



I. : Resonance or delocalisation of lone pair of electrons on benzene ring occur that decreases basicity.

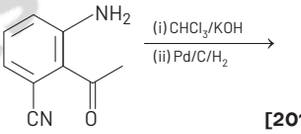


IV. : Strong resonance or delocalisation of lone pair of electron on nitrogen.The electron pair is a part of aromatic 6 electron system.

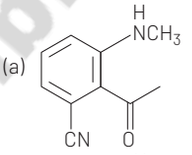
∴ Least basic among given options.

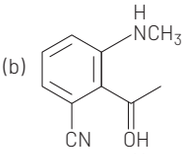
So, the correct order of basicity is III > II > I > IV

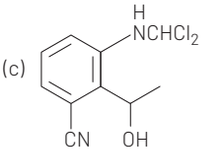
74 The major product obtained in the following reaction is

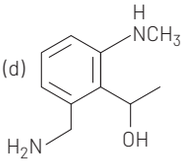


[2019, 8 April Shift-II]

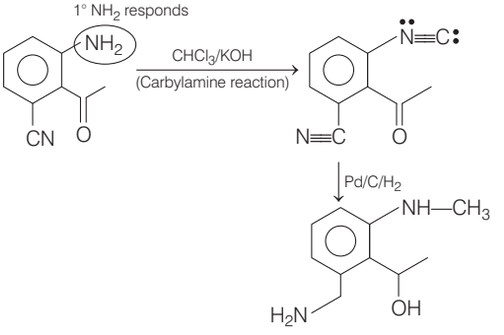
(a) 

(b) 

(c) 

(d) 

Ans. ***(d)***



In step (i), 1° amine is converted into isocyanide, when reacts with $CHCl_3$/KOH. This reaction is known as carbylamine reaction. This reaction is used to detect primary amine in a compound.

In step (ii), isocyanide is reduced to secondary amine and cyanide is reduced to primary amine, and carbonyl group to alcoholic group when treated with Pd/C/H_2.

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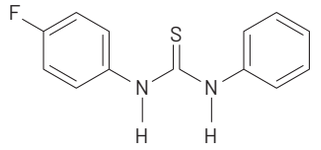
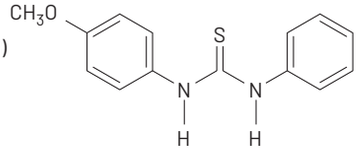
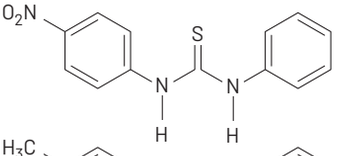
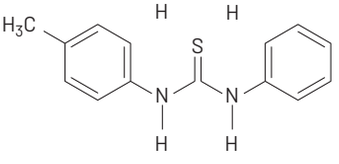
75 The increasing order of the pK_b of the following compound is **[2019, 12 April Shift-I]**

(A) 

(B) 

(C) 

(D) 

(a) (A) < (C) < (D) < (B) (b) (C) < (A) < (D) < (B)

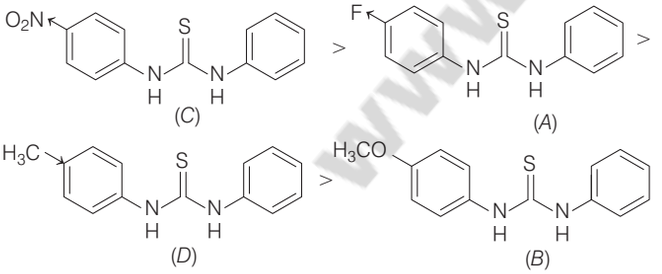
(c) (B) < (D) < (A) < (C) (d) (B) < (D) < (C) < (A)

Ans. ***(c)***

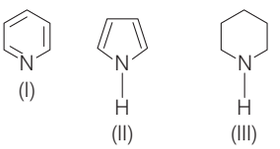
Key Idea pK_b value is defined as the minus logarithm of K_b. Smaller the value of pK_b, stronger is the base and *vice-versa*.

In the given options, *+R* effect is shown by —CH_3 and —OCH_3 group (—OCH_3 > —CH_3). These group increases the electron density at *o* and *p*-positions. Groups such as —F and —NO_2 shows *-R*-effect (—NO_2 > —F). These group decreases the electron density at *o* and *p*- positions.

Increase in electron density at *p*-position makes the unshared electron pair of '*N* ' more available and decrease in electron density at *p*-position makes the unshared electron pair of '*N* ' less available. Compound containing —OCH_3 group act as strongest base and hence possess lowest value of pK_b. So, the correct increasing order of pK_b in the given compound is



76 Arrange the following amines in the decreasing order of basicity : **[2019, 9 Jan Shift-I]**



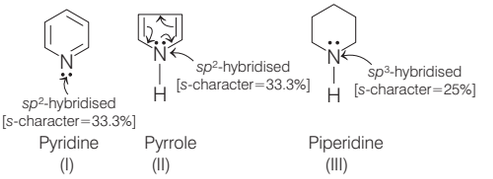
(a) I > II > III (b) III > II > I (c) I > III > II (d) III > I > II

Ans. ***(d)***

Key Idea Basicity ∝ Ease of donation of lone pair of electrons

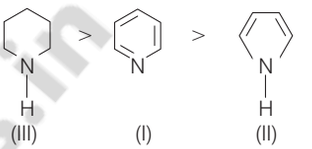
$$\propto \frac{1}{\%\text{ of s- character of N}} \propto \frac{1}{\text{Electronegativity of N}}$$

The % of *s*-character in the given amines are as follows:

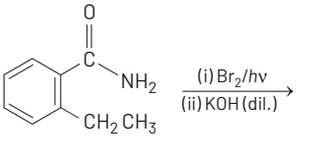


Therefore, piperidine (III) having minimum % s-character is most basic. Among the rest, pyridine (I) and pyrrole (II) the lone pair of electrons of N in pyrrole (II) is involved in delocalisation and follows $(4n+2)\ \pi$ aromatic ($n = 1$) system. So, the N-atom of pyrrole (II) will show least basicity.

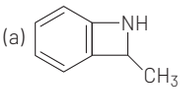
Thus, the order of basicity is as follows:

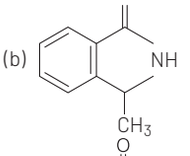


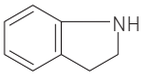
77 The major product of the following reaction is

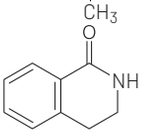


[2019, 9 Jan Shift-II]

(a) 

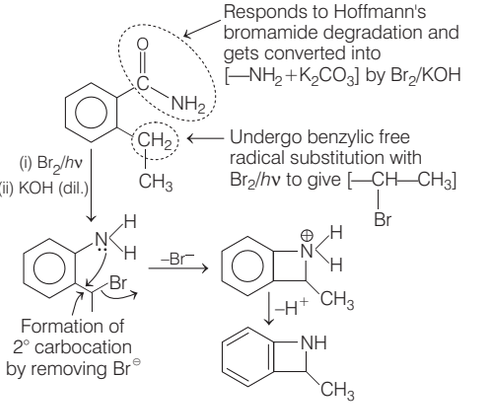
(b) 

(c) 

(d) 

Ans. ***(a)***

In the given reaction,



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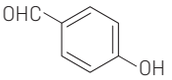
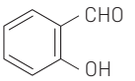
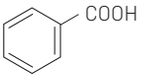
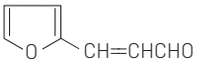
78 An aromatic compound '*A*' having molecular formula $C_7H_6O_2$ on treating with aqueous ammonia and heating forms compound '*B*'. The compound '*B*' on reaction with molecular bromine and potassium hydroxide provides compound '*C*' having molecular formula C_6H_7N. The structure of '*A*' is

(a) 

(b) 

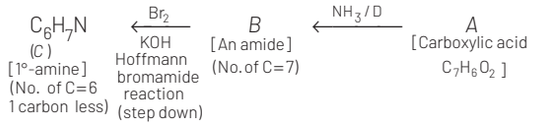
(c) 

(d) 

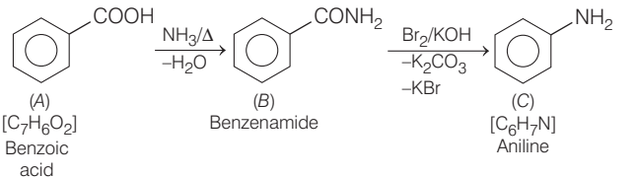
[2019, 10 Jan Shift-II]

Ans. ***(c)***

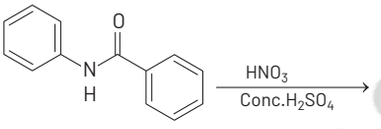
Using retro-synthesis, to get the required compounds, *A*, *B* and *C*.

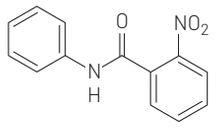


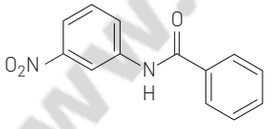
So, the reactions can be shown as:

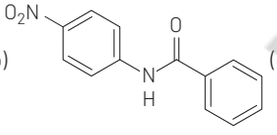


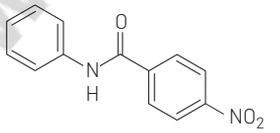
79 What will be the major product in the following mononitration reaction ?



(a) 

(c) 

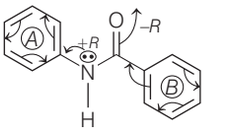
(b) 

(d) 

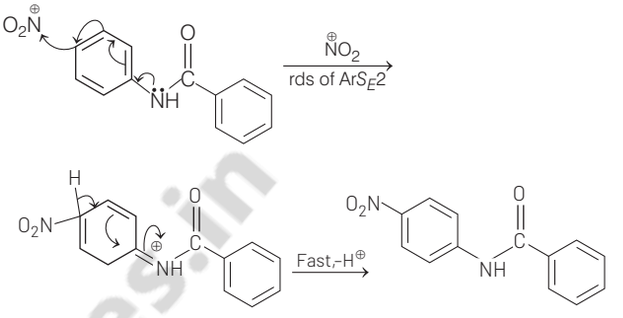
[2019, 10 Jan Shift-II]

Ans. ***(b)***

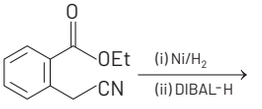
Here, in mononitration the electrophile produced from mixed acid (HNO_3 + conc.H_2SO_4) is $\overset{+}{N}O_2$.

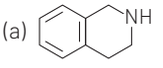


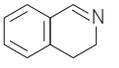
Ring-(*A*) is activated, i.e. becomes more nucleophilic by the + *R* effect of the —$\ddot{N}$H— group and it becomes *o* / *p*-directing towards the electrophile, NO_2^+ in the ArS_E2 reaction. For mononitration, $\overset{\oplus}{N}O_2$ will preferably come at *p*-position, whereas the ring-(*B*) gets deactivated by –*R*- effect of the —C(=O)— group,

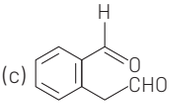


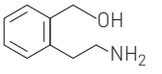
80 The major product of the following reaction is



(a) 

(b) 

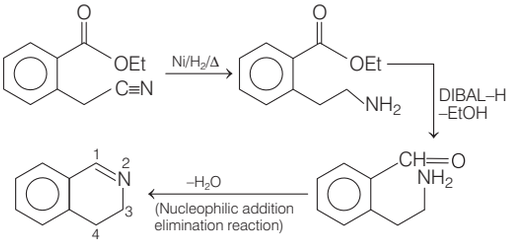
(c) 

(d) 

[2019, 11 Jan Shift-I]

Ans. ***(b)***

Ni/H_2 can reduce –C ≡ N into —CH_2—NH_2 (1°-amine) but cannot reduce an ester group (—CO_2Et) whereas DIBAL-H, di-isobutylaluminium hydride, $[(CH_3)_2CH]_2AlH$ reduces the ester group (—CO_2Et) into –CHO (an aldehyde) and C_2H_5OH.



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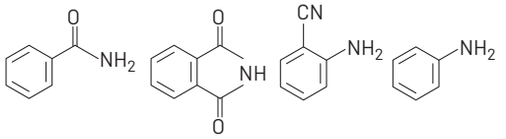
81 The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is **[2019, 12 Jan Shift-I]**



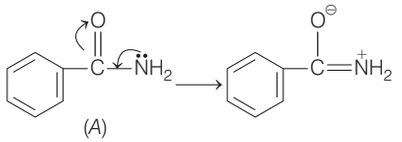
(A) (B) (C) (D)

(a) $(A)<(C)<(D)<(B)$ (b) $(B)<(A)<(C)<(D)$
(c) $(B)<(A)<(D)<(C)$ (d) $(A)<(B)<(C)<(D)$

Ans. ***(b)***

The reaction of alkyl halide with amine or amides is a nucleophilic substitution reaction.

More nucleophilic nitrogen is more reactive with alkyl halide. Compound (*A*) is benzamide and lone pair of 'N' of it, is not available in this compound.



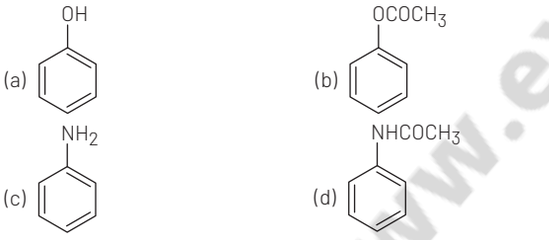
(A)

In compound (*D*), lone pair of 'N' are available but in compound (*C*), the lone pair of 'N' are not readily available due to the presence of electron withdrawing group (—CN) attach to benzene ring.

In compound (*B*), i.e. pthalimide, 'N' is not nucleophilic due to the presence of two polar groups attached to it that pulls lone pair towards them.

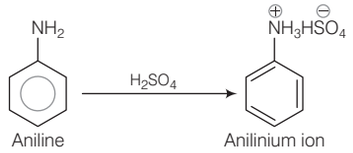
Hence, the correct order is : $(B)<(A)<(C)<(D)$.

82 Which of the following compounds will give significant amount of *meta*-product during mononitration reaction? **[JEE Main 2017]**



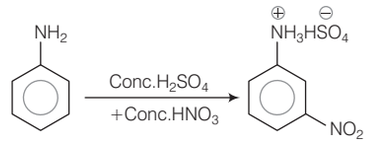
Ans. ***(c)***

Aniline in presence of nitrating mixture (conc. HNO_3 + conc. H_2SO_4) gives significance amount ($\approx 47\%$) of meta-product because in presence of H_2SO_4 its protonation takes place and anilinium ion is formed.



Aniline Anilinium ion

Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.

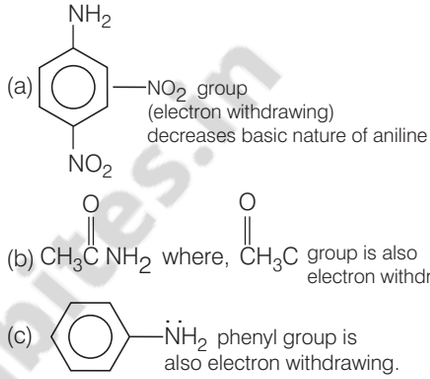


83 Amongst the following the most basic compound is **[AIEEE 2005]**

(a) *p* -nitroaniline (b) acetanilide
(c) aniline (d) benzylamine

Ans. ***(d)***

Basic nature of the compound is related to their tendency to donate their lone pair of electrons more readily. – *I* effect [e^- withdrawing] exerting group decreases the basic strength while + *I* effect [e^- donating] exerting group increases the basic strength of the compound.



(a) NO_2 group (electron withdrawing) decreases basic nature of aniline

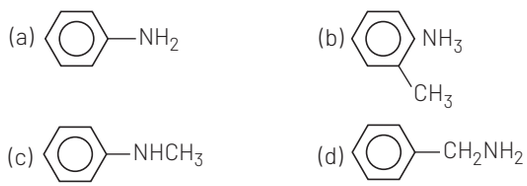
(b) $CH_3\overset{O}{\overset{\|}{C}}NH_2$ where, $CH_3\overset{O}{\overset{\|}{C}}$ group is also electron withdrawing

(c) $\ddot{N}H_2$ phenyl group is also electron withdrawing.

(d) Benzylamine ($C_6H_5CH_2NH_2$) contains alkyl group linked to amine, —NH_2 group. This alkyl group is + I effect [e^- donating] exerting group which increases the basicity of benzylamine.

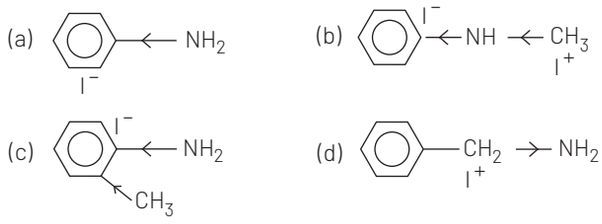
Thus, most basic compound is benzylamine.

84 Which of the following is the strongest base? **[AIEEE 2004]**



Ans. ***(d)***

CH_3—[an electron releasing (+ *I*) group] increases electron density at N-atom, hence basic nature is increased.



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C_6H_5 decreases electron density at N-atom due to delocalisation of e^- of NH_2 with πe^- of benzene. Thus, basic nature is decreased.

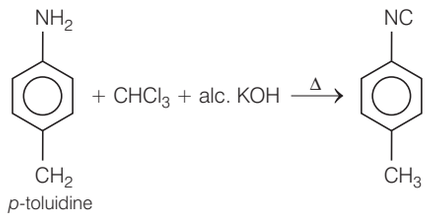
Hence, (d) is the strongest base.

85 The reaction of chloroform with alcoholic KOH and *p* -toluidine form **[AIEEE 2003]**

(a) H_3C—⬡—CN (b) H_3C—⬡—N_2Cl

(c) H_3C—⬡—$NHCHCl_2$ (d) H_3C—⬡—CN

Ans. ***(c)***

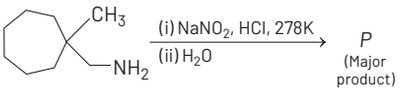


p-toluidine

This is carbylamine reaction.

TOPIC 3
Diazonium Salts

86 What is the major product *P* of the following reaction ?



[2021, 25 July Shift-II]

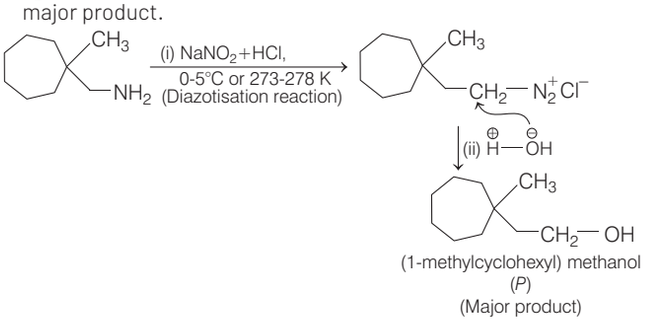
(a) ⬡(CH3)(CH3) (b) ⬡(CH3)(Cl)

(c) ⬡(OH)($N_2^{\oplus}Cl^{\ominus}$) (d) ⬡(CH3)(OH)

Ans. ***(d)***

In first step, $NaNO_2$, HCl is used for diazotisation reaction at 0-5°C. In last step, H_2O is used as a nucleophilic substitution of N_2 (leaving group).

N_2 is best leaving group to form (1-methylcyclohexyl) methanol as major product.



87 $C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow[H^+]{C_6H_5N_2^+Cl^-} P$ (Yellow coloured compound)

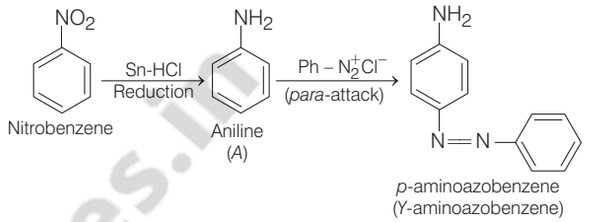
Consider the above reaction, the product *P* is **[2021, 25 July Shift-II]**

(a) ⬡(N=N)(NH2) (b) ⬡(N=N)—⬡(NH2)

(c) ⬡(N)—N—⬡ (d) ⬡(H)—N=N—N—⬡

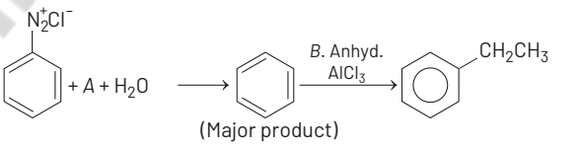
Ans. ***(b)***

Sn — HCl is used for reduction of — NO_2 group into — NH_2 group. On next step, $PhN_2^+Cl^-$ is used to form yellow coloured azo dye with aniline. This is a coupling reaction.



Due to its various resonating structures, there's an excess of electron or negative charge over *ortho* and *para* positions of the benzene ring than the *meta*-position. Thus, anilines are *o* and *p*-directing towards electrophilic substitution reactions.

88



In the chemical reactions given above *A* and *B* respectively are **[2021, 22 July Shift-II]**

(a) H_3PO_2 and CH_3CH_2Cl (b) CH_3CH_2OH and H_3PO_2

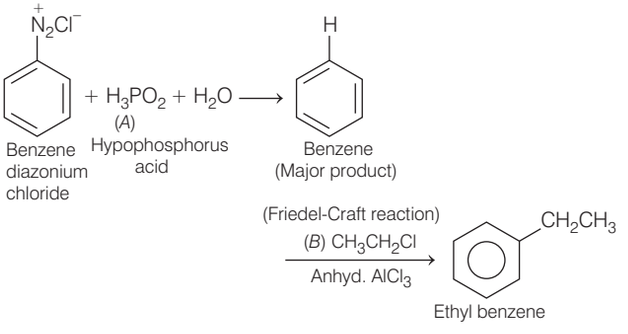
(c) H_3PO_2 and CH_3CH_2OH (d) CH_3CH_2Cl and H_3PO_2

Ans. ***(a)***

H_3PO_2 is compound A and CH_3CH_2Cl is compound *B*.

When benzene diazonium chloride reacts with H_3PO_2 (hypophosphorus acid) and water gives benzene (major product) which on reaction with ethyl chloride in presence of anhydrous $AlCl_3$ gives ethyl benzene.

Chemical reaction is as follows ;



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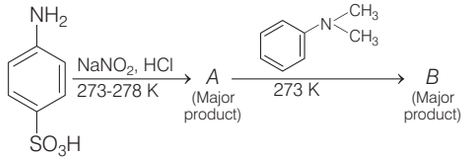
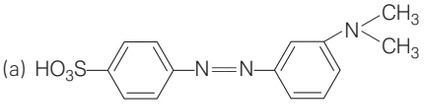
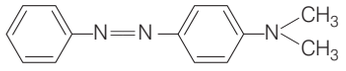
89

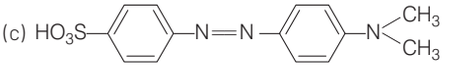


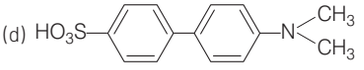
Consider the above reaction, compound *B* is

[2021, 20 July Shift-II]

(a) 

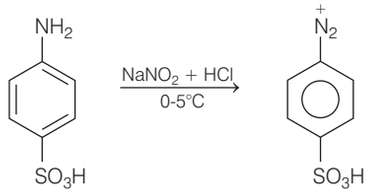
(b) 

(c) 

(d) 

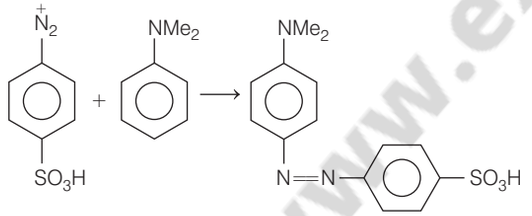
Ans. ***(c)***

Diazonium salt is formed on treating an amine with $NaNO_2$ / HCl at low temperature.

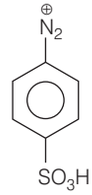


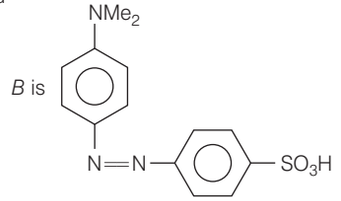
A (Major product)

Diazonium salt on treating with a N,N-dimethylaniline gives an azo compound. N, N-dimethyl aniline forms bond with N at *para*-position as amine group is a *o*, *p*-directing group.



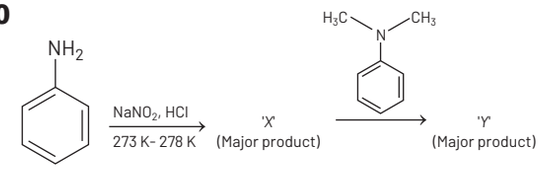
B (Major product)
(Azo compound)

Therefore, *A* is  *para*-diazosulphonic acid

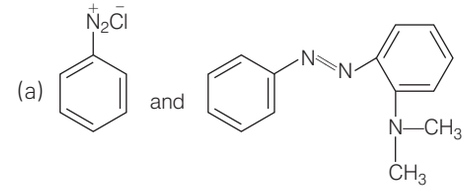
B is 

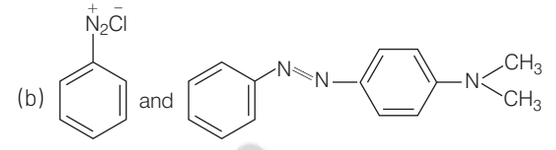
para (N,N-dimethylaminophenyl Benzene sulphonic acid

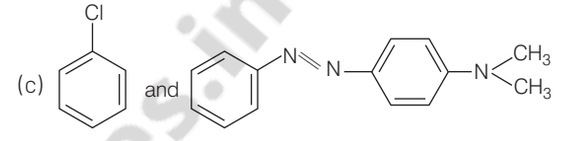
90

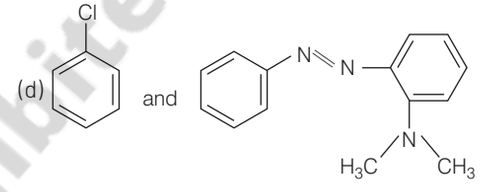


[2021, 18 March Shift-I]

(a) 

(b) 

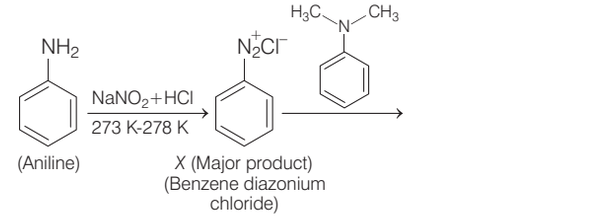
(c) 

(d) 

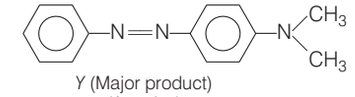
Ans. ***(b)***

Aniline reacts with sodium nitrite and HCl in cold condition to form benzene diazonium chloride (*X*) and on further reaction, it form azo dye (*Y*).

Chemical reactions are as follows

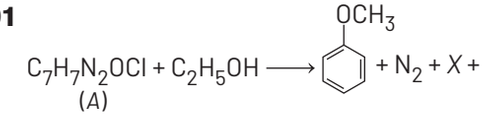


(Aniline) *X* (Major product) (Benzene diazonium chloride)



Y (Major product)
(Azo dye)

91



In the above reaction, the structural formula of (*A*), *X* and *Y* respectively are

[2021, 17 March Shift-II]

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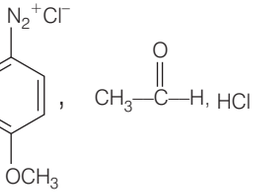
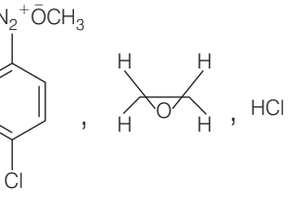
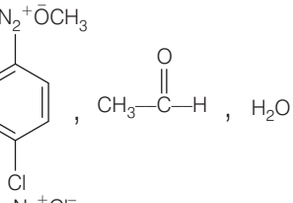
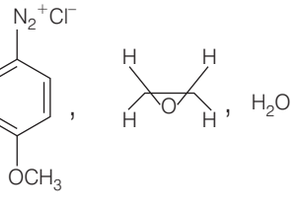
(a)  ,

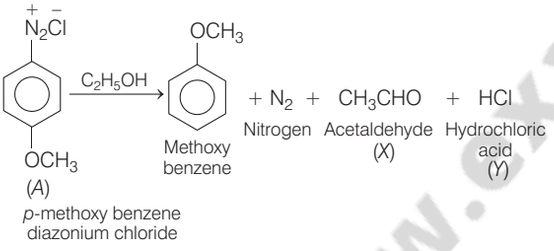
(b) 

(c) 

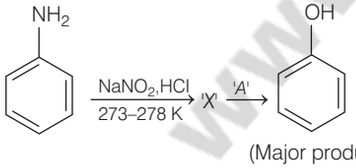
(d) 

Ans. ***(a)***

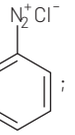
The structural formula of (*A*), *X* and *Y* are *p*-methoxy benzene diazonium chloride, acetaldehyde and hydrochloric acid respectively. Reaction involved are as follows

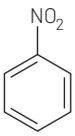


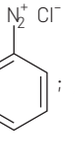
92

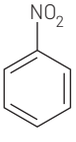


In the above chemical reaction, intermediate *X* and reagent / condition *A* are **[2021, 16 March Shift-I]**

(a) *X*-  ; *A* -H_2O/NaOH

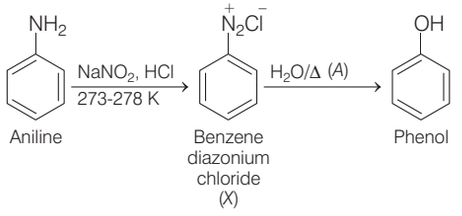
(b) *X*-  ; *A* -H_2O/Δ

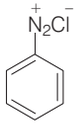
(c) *X*-  ; *A* -H_2O/Δ

(d) *X*-  ; *A* -H_2O/NaOH

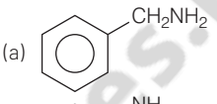
Ans. ***(c)***

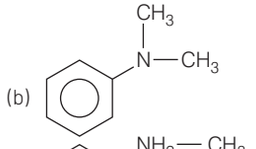
Aniline reacts with $NaNO_2$, HCl at 273-278 K to give benzene diazonium salt ($C_6H_5\overset{+}{N}_2\overset{-}{Cl}$ = *X*) which on hydrolysis (H_2O/Δ) gives phenol. Complete reaction is as follows

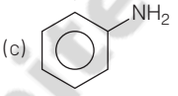


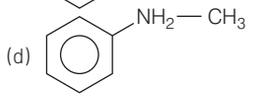
So, *X* =  and *A* = H_2O/Δ

93 The diazonium salt of which of the following compounds will form a coloured dye on reaction with β-naphthol in NaOH ? **[2021, 24 Feb Shift-II]**

(a) 

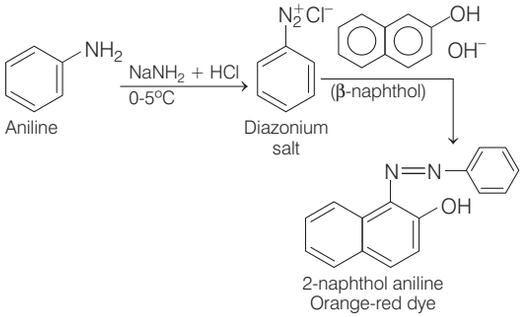
(b) 

(c) 

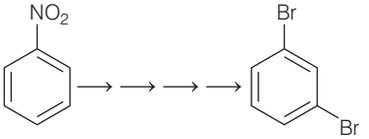
(d) 

Ans. ***(c)***

Initially aniline reacts with diazotisation reagent to form diazonium salt. Then β-naphthol react with salt and orange-red dye is obtained. So, diazonium salt of aniline is used to prepare orange-red dye.



94 What is the correct sequence of reagents used for converting nitrobenzene into *m*-dibromobenzene?



[2021, 24 Feb Shift-II]

(a) $\xrightarrow{NaNO_2}$ / $\xrightarrow{HCl}$ / $\xrightarrow{KBr}$ / $\xrightarrow{H^+}$

(b) $\xrightarrow{Br_2/Fe}$ / $\xrightarrow{Sn/HCl}$ / $\xrightarrow{NaNO_2/HCl}$ / $\xrightarrow{CuBr/HBr}$

(c) $\xrightarrow{Sn/HCl}$ / $\xrightarrow{KBr}$ / $\xrightarrow{Br_2}$ / $\xrightarrow{H^+}$

(d) $\xrightarrow{Sn/HCl}$ / $\xrightarrow{Br_2}$ / $\xrightarrow{NaNO_2}$ / $\xrightarrow{NaBr}$

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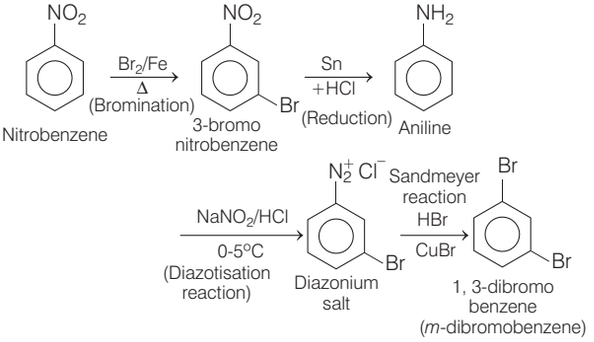
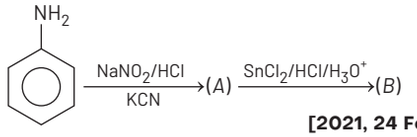
Ans. ***(b)***

In first step, NO_2 group is electron withdrawing group, it decreases the electron density in *meta* position and bromination occur in *meta* position. In second step, Sn/HCl used for reduction to convert —NO_2 to —NH_2 and form aniline. In next step, diazonium salt is formed and at last bromine replace $N_2^+Cl^-$ group to form 1, 3-dibromobenzene.

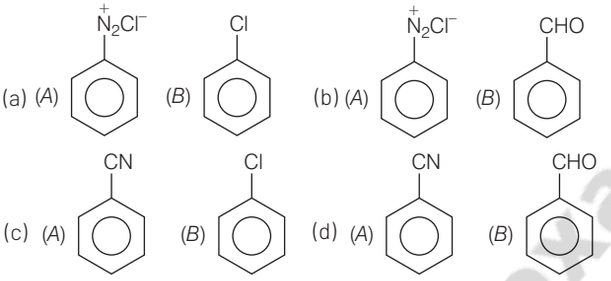
Complete reaction is as follows



95 '*A*' and '*B*' in the following reaction are

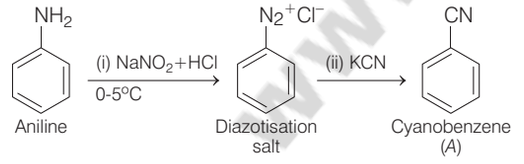


[2021, 24 Feb Shift-I]

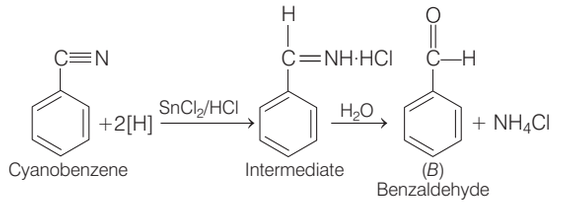


Ans. ***(d)***

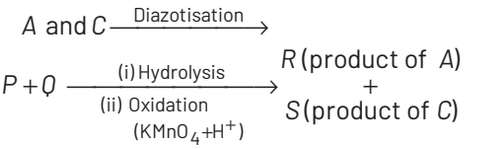
Step 1 In step 1, $NaNO_2$ + HCl , 0-5°C used for diazotisation reaction. It will form diazonium salt. Further, it will react with KCN to form cyanobenzene.



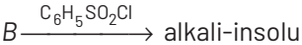
Step 2 In step 2, $SnCl_2$ and HCl is a Stephen's reduction reagent. Cyanobenzene reduced to benzaldehyde by $SnCl_2$/HCl.



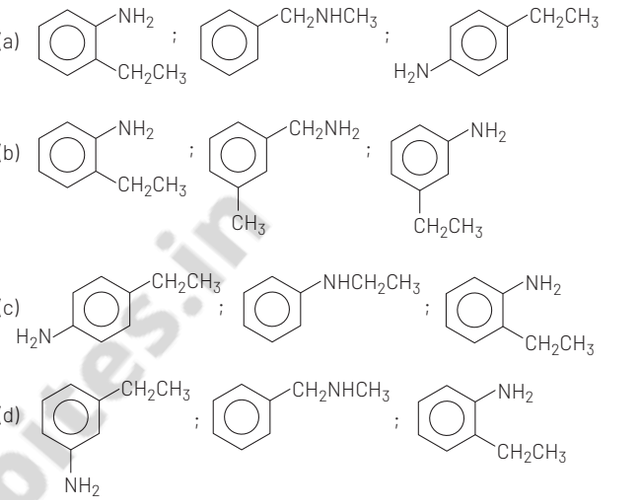
96 Three isomers *A*,*B* and *C* (molecular formula $C_8H_{11}N$) give the following results :



R has lower boiling point than *S*.

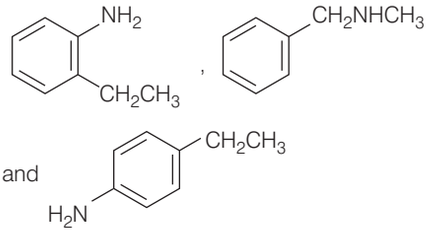


A, *B* and *C*, respectively are **[2020, 3 Sep Shift-II]**

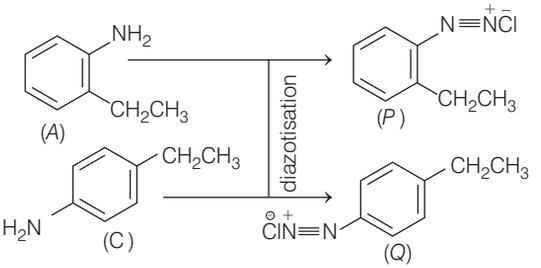


Ans. ***(a)***

A, *B* and *C* respectively are



According to the question, *A* and *C* undergoes diazotisation to give *P* and *Q*. So, amine must be primary aromatic amine.



Which on hydrolysis followed by oxidation gives alcohol derivative.

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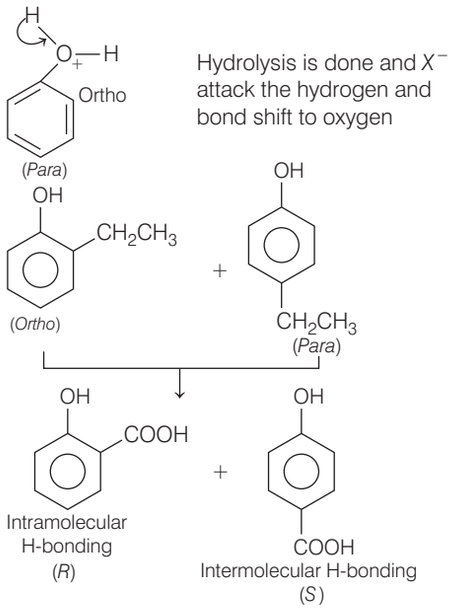


Given, *R* has low boiling point than *S*. Intramolecular H-bond is weaker than intermolecular H-bond.

It means intramolecular H-bonding show low boiling point and here, *R* is *ortho* product and *S* is *para* product.

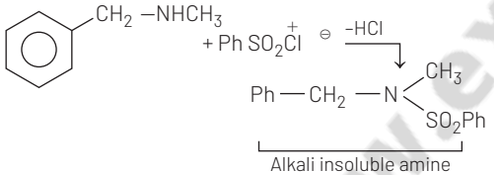
Given, $(B) \xrightarrow{C_6H_5SO_2Cl}$ alkali-insoluble product

$C_6H_5SO_2Cl$ act as electrophile then *B* must be amine.

Secondary amine act as a nucleophile.

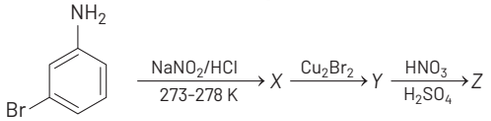
The $C_6H_5SO_2Cl$ act as electrophile and displace Cl.

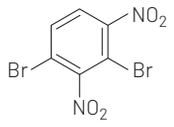
In the given option (b), secondary amine is present in the reaction takes place as follows :

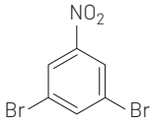


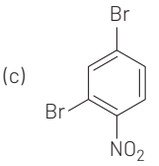
Primary and secondary amine forms poorly soluble ppt. on reaction with $PhSO_2Cl$.

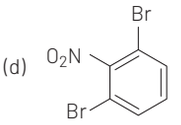
97 The major product *Z* obtained in the following reaction scheme is **[2020, 9 Jan Shift-I]**



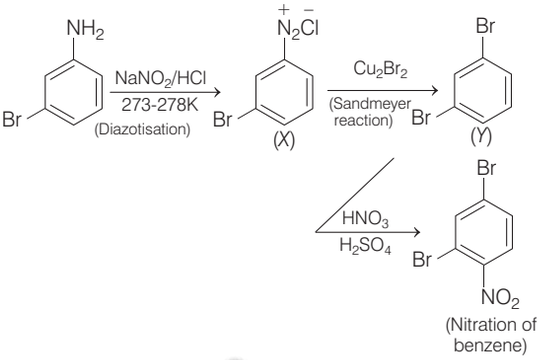
(a) 

(b) 

(c) 

(d) 

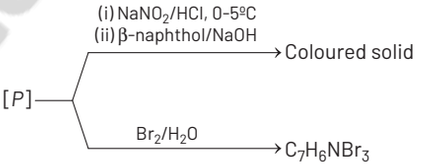
Ans. ***(c)***



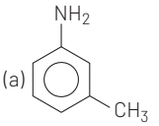
Br is *o, p*-directing group.

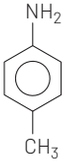
$\therefore$ NO_2 is attached at the *ortho* position of one of the Br atoms which is also *para* position with respect to the other Br atom.

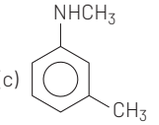
98 Consider the following reactions :

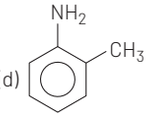


The compound [*P*] is **[2020, 9 Jan Shift-II]**

(a) 

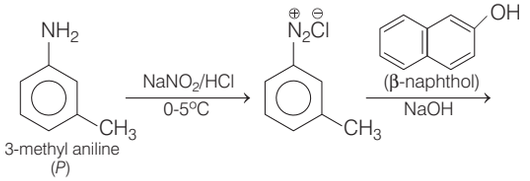
(b) 

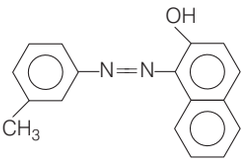
(c) 

(d) 

Ans. ***(a)***

Compound [*P*] is 3-methylaniline.
Complete reaction is as follows :




(Coloured azo dye)

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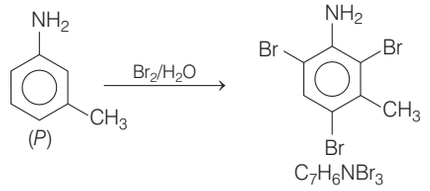
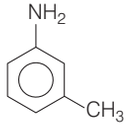
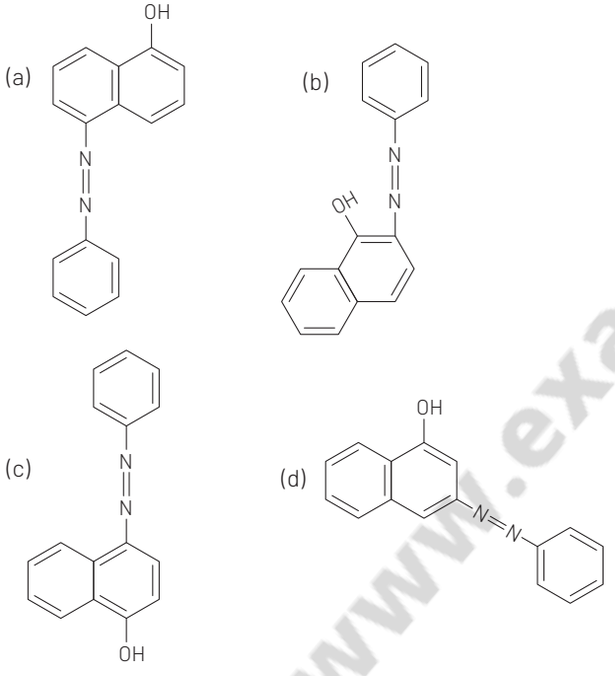


On comparing the formula $C_7H_6NBr_3$ with the formula of *m*-methylaniline (C_7H_9N), it is noticed that, three H atoms are substituted with three Br atoms (tribromination). To get a tribrominated product, all three activated positions of aniline (2 *ortho* and one *para*) must be free, where Br can come.

Then, it can be concluded that the methyl group must be at *meta*-position only.

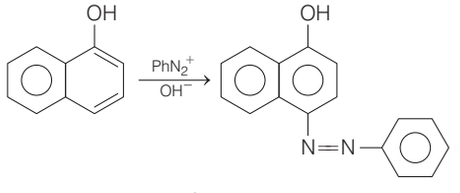


99 Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give **[2019, 8 April Shift-I]**

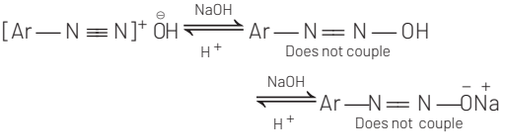


Ans. ***(c)***

Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give the following coupling reaction.



In the presence of $O\bar{H}$ ion, ArN_2^+ exists in equilibrium with an unionised compound ($Ar-N=N-OH$) and salts $[ArN=N^+]^-\ \ominus\!\!-OH$ derived from it, which do not couple.

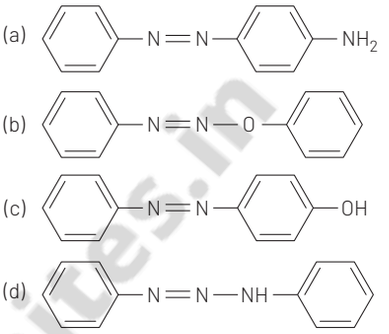


Following conditions are very useful for coupling reaction to take place.

(a) The solution must be so alkaline that the concentration of diazonium ion is too low.

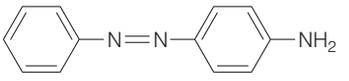
(b) It must not be so acidic that the concentration of free phenoxide ion is too low.

100 Aniline dissolved in dil. HCl is reacted with sodium nitrite at 0°C. This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil. HCl. The structure of the major product is **[2019, 9 April Shift-I]**



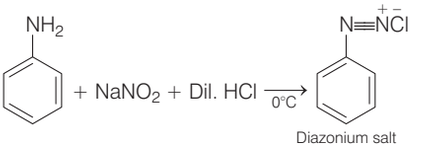
Ans. ***(a)***

Major product of the reaction is

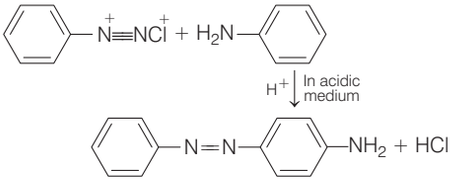


It is obtained by coupling reaction.

Reaction of aniline with dil. HCl and sodium nitrite at 0°C is shown below :



Diazonium salt formed when added to equimolar mixture of aniline and phenol in dil. HCl then aniline couples with diazonium salt. Reaction is as follows :



For an effective coupling, the solution must be so alkaline that the concentration of diazonium ion is too low. It must not be so acidic that the concentration of free amine or phenoxide ion is too low. That is why amines couple fastest in mild acidic solution and phenols couple fastest in mild alkaline solution.

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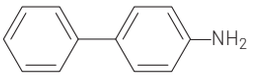
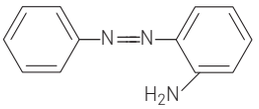
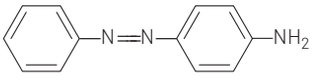
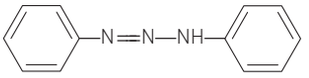
101 Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid gives **[2019, 12 April Shift-II]**

(a) 

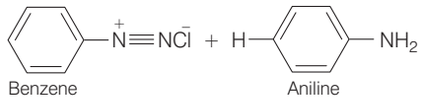
(b) 

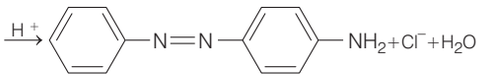
(c) 

(d) 

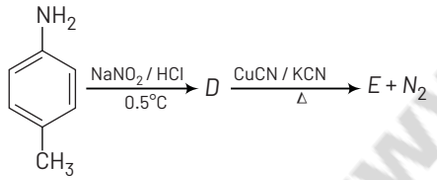
Ans. ***(c)***

Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid undergoes coupling reaction and produces *p*-amino azobenzene. In this reaction, benzene diazonium chloride reacts with aniline in which aniline molecule at its *para*-position is coupled with diazonium salt to give *p*-amino azobenzene (yellow dye).

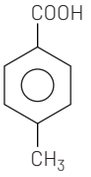


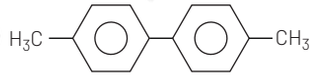


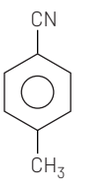
102 In the reaction,

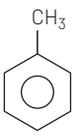


The product *E* is **[JEE Main 2015]**

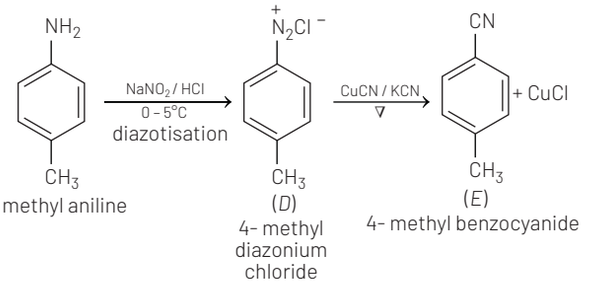
(a) 

(b) 

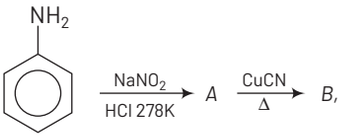
(c) 

(d) 

Ans. ***(c)***



103 In the chemical reaction,



compounds *A* and *B* respectively are

(a) fluorobenzene and phenol **[AIEEE 2011]**

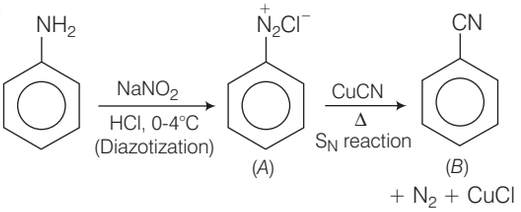
(b) benzene diazonium chloride and benzonitrile

(c) nitrobenzene and chlorobenzene

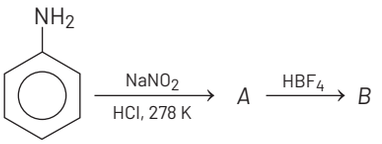
(d) phenol and bromobenzene

Ans. ***(b)***

Formation of *A* is by diazotisation and formation of *B* from *A* is by S_N reaction. Thus, the complete series of reaction is given by



104 In the chemical reaction, **[AIEEE 2010]**



the compounds '*A*' and '*B*' respectively are

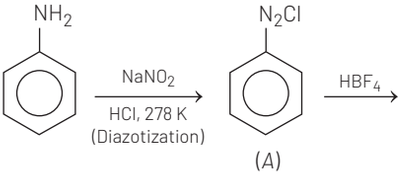
(a) nitrobenzene and fluorobenzene

(b) phenol and benzene

(c) benzene diazonium chloride and fluorobenzene

(d) nitrobenzene and chlorobenzene

Ans. ***(c)***



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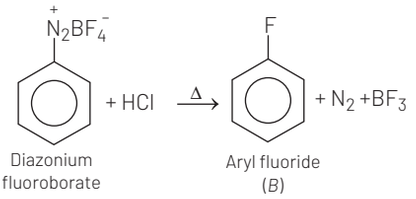
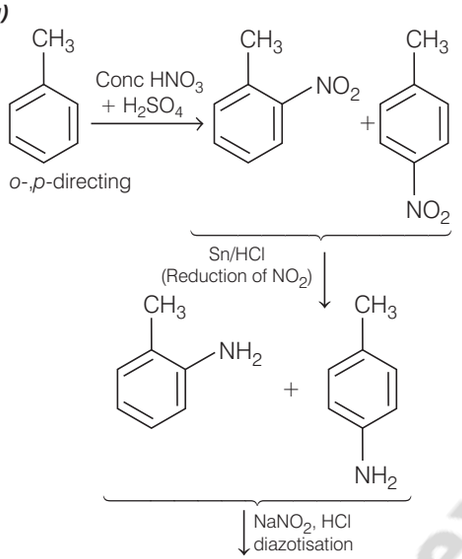


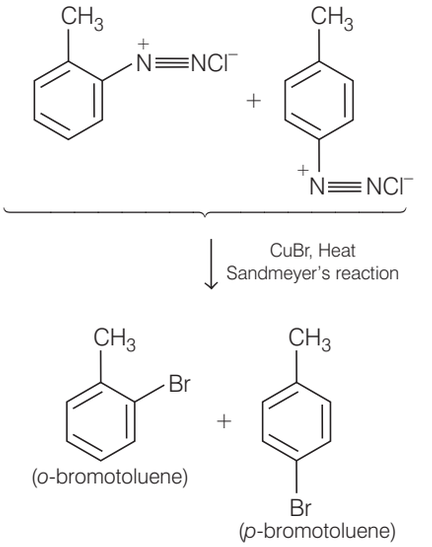
The reaction of diazonium chloride with fluoroboric acid (HBF_4) is called Balz-Schiemann reaction.

105 Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains **[AIEEE 2008]**

(a) mixture of *o*-and *p*-bromotoluenes
(b) mixture of *o*-and *p*-dibromobenzenes
(c) mixture of *o*-and *p*-bromoanilines
(d) mixture of *o*-and *m*-bromotoluenes

Ans. ***(a)***

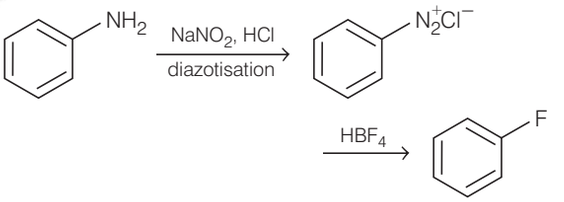




106 Fluorobenzene (C_6H_5F) can be synthesized in the laboratory **[AIEEE 2006]**

(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4
(c) by direct fluorination of benzene with F_2 gas
(d) by reacting bromobenzene with NaF solution

Ans. ***(b)***



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27
Polymers

TOPIC 1
Classification of Polymers

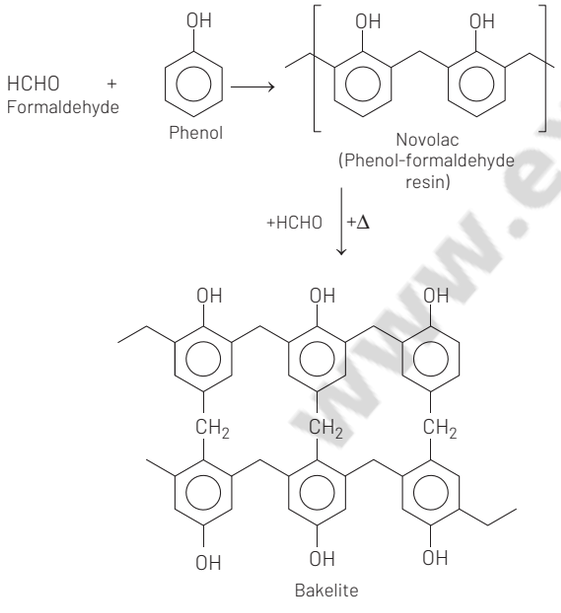
01 The polymer formed on heating novolac with formaldehyde is **[2021, 26 Aug Shift-I]**

(a) bakelite
(b) polyester
(c) melamine
(d) nylon 6,6

Ans. ***(a)***

Novolac + Formaldehyde $\xrightarrow{\Delta}$ Bakelite

Novolac when heated with formaldehyde will undergoes cross linking to form an infusible solid mass called bakelite.

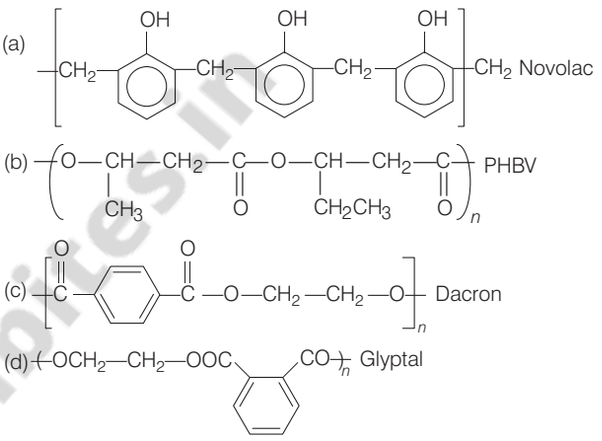


02 Which among the following is not a polyester ? **[2021, 31 Aug Shift-II]**

(a) Novolac
(b) PHBV
(c) Dacron
(d) Glyptal

Ans. ***(a)***

The structure of the given polymers are as follows



∵ Novolac does not contain any ester group.

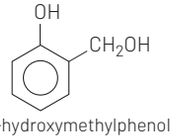
∴ It is not a polyester.

03 Monomer of novolac is **[2021, 31 Aug Shift-I]**

(a) 3-hydroxybutanoic acid
(b) phenol and melamine
(c) *o*-hydroxymethylphenol
(d) 1,3-butadiene and styrene

Ans. ***(c)***

The monomer of novolac is *o*-hydroxymethylphenol.



o-hydroxymethylphenol

Hence, correct option is (c).

04 Staggered and eclipsed conformers of ethane are **[2021, 27 July Shift-I]**

(a) polymers
(b) rotamers
(c) enantiomers
(d) mirror images

Ans. ***(b)***

Rotamers are isomers of a molecule which can be interconverted by rotation of a part of molecule about a particular bond.

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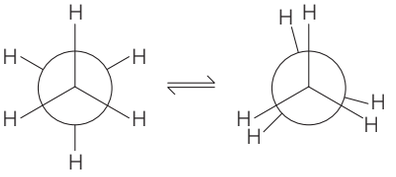
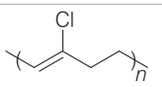
Conformational isomerism is a form of stereo isomerism in which isomers can be inter converted just by rotation about formally single bonds.



Staggered ($\theta = 60^\circ$) (More stable) ⇌ Eclipsed ($\theta = 0^\circ$) (Less stable)

05 Match List I with List II.

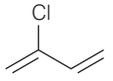
	List I		List II
(A)	Chloroprene	(i)	
(B)	Neoprene	(ii)	
(C)	Acryonitrile	(iii)	
(D)	Isoprene	(iv)	$CH_2 = CH—CN$

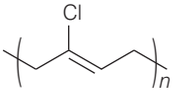
Choose the correct answer from the options given below. **[2021, 22 July Shift-II]**

	A	B	C	D
(a)	(iii)	(iv)	(ii)	(i)
(b)	(ii)	(iii)	(iv)	(i)
(c)	(ii)	(i)	(iv)	(iii)
(d)	(iii)	(i)	(iv)	(ii)

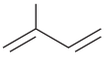
Ans. ***(b)***

Correct matches are as follows :

(A) Chloroprene 

(B) Neoprene 

(C) Acrylonitrile $CH_2 = CH—CN$

(D) Isoprene 

(Neoprene is produced by free radical polymerisation of chloroprene)

Hence, (A)-(ii), (B)-(iii), (C)-(iv), (D)-(i).

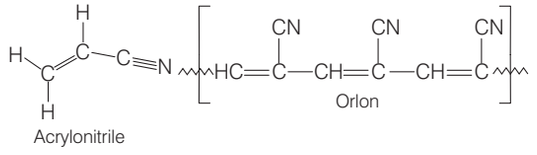
06 Orlon fibres are made up of **[2021, 20 July Shift-I]**

(a) polyacrylonitrile (b) polyester
(c) polyamide (d) cellulose

Ans. ***(a)***

Orlon is the commercial name for polyacrylonitrile.

Therefore, it is the polymer of acrylonitrile.



Acrylonitrile — Orlon

07 Match List-I with List-II.

	List-I (Chemicals)		List-II (Use / Preparation / Constituent)
(A)	Alcoholic potassium hydroxide	(i)	Electrodes in batteries
(B)	$Pd/BaSO_4$	(ii)	Obtained by addition reaction
(C)	BHC (Benzene hexachloride)	(iii)	Used for β-elimination reaction
(D)	Polyacetylene	(iv)	Lindlar catalyst

Choose the most appropriate match **[2021, 18 March Shift-I]**

	A	B	C	D
(a)	(ii)	(i)	(iv)	(iii)
(b)	(iii)	(iv)	(ii)	(i)
(c)	(iii)	(i)	(iv)	(ii)
(d)	(ii)	(iv)	(i)	(iii)

Ans. ***(b)***

(A) Alcoholic KOH is used for β - elimination reaction. It will form alkane as a major product.

(B) $Pd/BaSO_4$ (Lindlar's catalyst) is used for convert alkyne to alkane.

(C) BHC (Benzene hexachloride) is used to obtained addition product of benzene and chlorine.

(D) Polyacetylene is used as electrodes in batteries.

∴ Correct match is (A-iii), (B-iv), (C-ii), (D-i).

08 Which of the following polymer is used in the manufacture of wood laminates? **[2021, 16 March Shift-II]**

(a) *cis*-polyisoprene
(b) Melamine formaldehyde resin
(c) Urea formaldehyde resin
(d) Phenol and formaldehyde resin

Ans. ***(c)***

Urea-formaldehyde is used to manufacture unbreakable cups and laminated sheets.

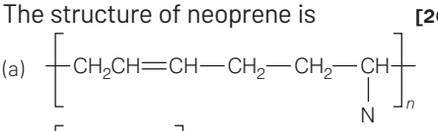
It is an example of condensation polymer in which water molecule is removed from urea and formaldehyde forming an amide linkage.

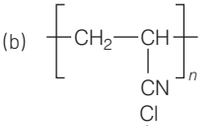
(a) *cis*-poly isoprene is natural rubber.

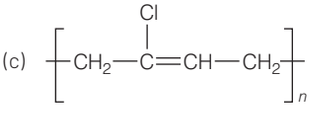
(b) Melamine - formaldehyde polymer used in the manufacture of unbreakable crockery.

(d) Phenol-formaldehyde resin used as good wood adhesives for plywood and particle board.

09 The structure of neoprene is **[2021, 26 Feb Shift-I]**

(a) 

(b) 

(c) 

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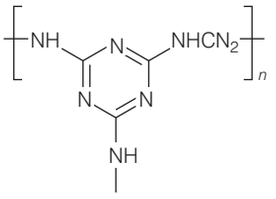
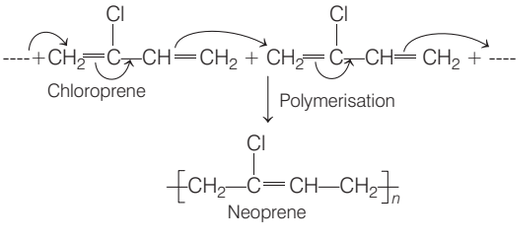
(d) 

Ans. ***(c)***

Neoprene is an addition homopolymer of chloroprene.



10 Which statement is correct? **[2021, 25 Feb Shift-I]**

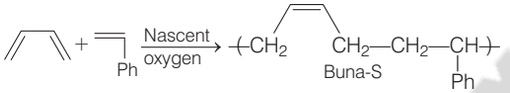
(a) Buna-N is a natural polymer.
(b) Buna-S is a synthetic and linear thermosetting polymer.
(c) Neoprene is an addition copolymer used in plastic bucket manufacturing.
(d) Synthesis of buna-S needs nascent oxygen.

Ans. ***(d)***

Only statement (d) is correct whereas other statements are incorrect. The correct statements are as follows

Buna-N is a synthetic polymer.

Buna-S is an elastomer. Buna-S is polymerised by addition polymerisation method, which needs radical initiator for chain propagation step. Nascent oxygen can be used as an radical initiator.



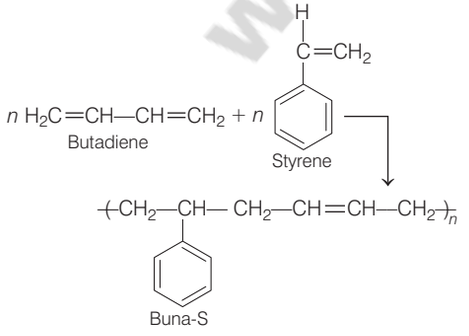
Neoprene is a synthetic rubber not an addition copolymer.

11 In polymer buna-S: 'S' stands for **[2021, 24 Feb Shift-II]**

(a) sulphonation (b) strength
(c) sulphur (d) styrene

Ans. ***(d)***

Buna-S is the co-polymer of but 1, 3-diene and styrene as follows.



Styrene butadiene rubber is also called buna-S, in which 'Bu' stands for butadiene, 'na' stands for sodium and 'S' stands for styrene.

Since, butadiene and styrene is one of the constituent monomer of given polymer.

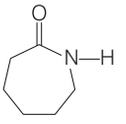
12 Match List-I with List-II.

	List-I (Monomer Unit)		**List-II** (Polymer)
A.	Caprolactum	1.	Natural rubber
B.	2-chloro buta-1,3-diene	2.	Buna-N
C.	Isoprene	3.	Nylon-6
D.	Acrylonitrile	4.	Neoprene

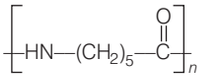
Choose the correct answer from the options given below **[2021, 24 Feb Shift-I]**

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	4	3	2	1
(c)	2	1	4	3	(d)	3	4	1	2

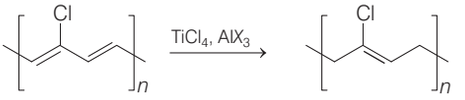
Ans. ***(d)***

(a) 

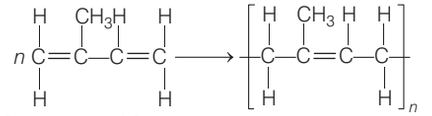
Caprolactum is the monomeric unit of polymer nylon-6



(b) 2-chlorobuta -1, 3-diene is the monomeric unit of polymer neoprene.

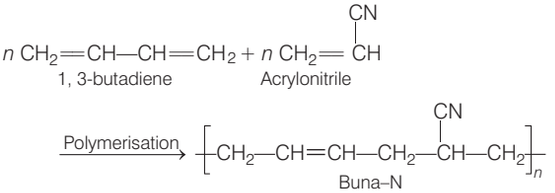


(c) 2-methylbuta-1, 3-diene (isoprene) is the monomeric unit of polymer natural rubber.



Value of *n* is about 10,000.

(d) CH_2=CH—CN (acrylonitrile) is one of the monomeric unit of polymer buna-N.



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13 The correct match between Item - I and Item - II is :

	Item - I		Item - II
(A)	Natural rubber	(I)	1,3- butadiene + styrene
(B)	Neoprene	(II)	1,3- butadiene + acrylonitrile
(C)	Buna -N	(III)	Chloroprene
(D)	Buna -S	(IV)	Isoprene

[2020, 6 Sep Shift-II]

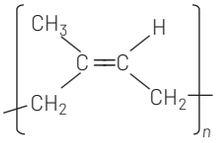
(a) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)
(b) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)
(c) (A)-(IV), (B)-(III), (C)-(II), (D)-(I)
(d) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)

Ans. ***(c)***

Correct match is (A)→(IV), (B)→(III), (C)→(II), (D)→(I)

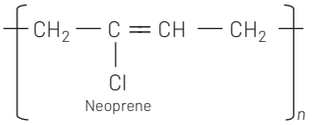
(a) $nCH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH_2 \longrightarrow$ Polycis-isoprene (Natural rubber)

Isoprene



(b) $nCH_2=\underset{\underset{Cl}{|}}{C}-CH=CH_2 \longrightarrow$

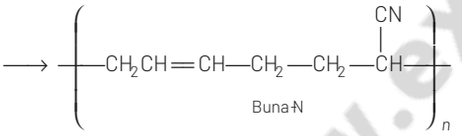
Chloroprene



Neoprene

(c) $nCH_2=CH-CH=CH_2 + nCH_2=\underset{\underset{CN}{|}}{CH}$

1, 3 butadiene — Acrylonitrile

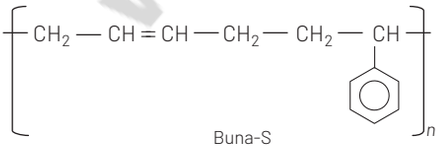


Buna-N

(d)

$nCH_2=CH-CH=CH_2 + nCH_2-CH \longrightarrow$

1, 3-butadiene — Styrene



Buna-S

Hence, option (c) is correct match.

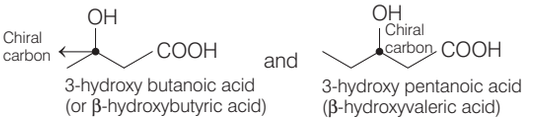
14 Which polymer has 'chiral' monomer?

[2020, 9 Jan Shift-II]

(a) PHBV (b) Buna-N
(c) Nylon 6, 6 (d) Neoprene

Ans. ***(a)***

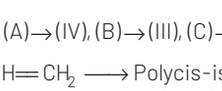
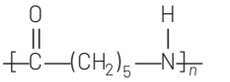
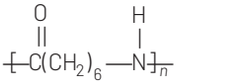
PHBV, (Poly 3- hydroxybutyrate -co-3- hydroxyvalerate) is a copolymer of



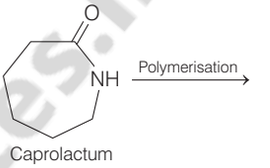
In both monomers, there is one chiral centre (shown by dark spot).

∴ Polymer contains chiral monomers.

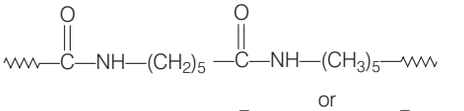
15 The structure of nylon-6 is **[2019, 8 April Shift-II]**

(a) 
(b) 
(c)
(d) 

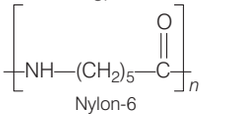
Ans. ***(b)***



Caprolactum



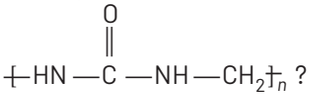
or



Nylon-6

Nylon-6 is prepared by ring opening polymerisation of caprolactum. It is heated about 533 K in an inert atmospheric nitrogen about 4-5 hrs. Nylon-6 fibres are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkle proof and highly resistant to abrasion and chemicals such as acids and alkalis.

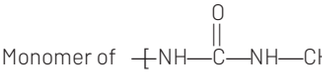
16 Which of the following compounds is a constituent of the polymer



[2019, 9 April Shift-II]

(a) *N*-methyl urea (b) Methylamine
(c) Ammonia (d) Formaldehyde

Ans. ***(d)***

Monomer of  is formaldehyde. The polymer is also known as urea-formaldehyde resin. It is made from urea (NH_2CONH_2) and formaldehyde (HCHO).

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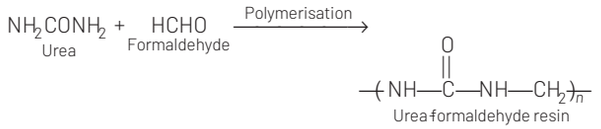


It is used for making unbreakable cups and laminated sheets.

17 Which of the following is a thermosetting polymer?
[2019, 12 April Shift-I]

(a) Bakelite (b) Buna-N (c) Nylon-6 (d) PVC

Ans. ***(a)***

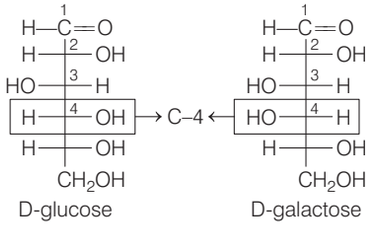
Bakelite is a thermosetting polymer. These polymers are cross-linked or heavily branched molecules which on heating undergo extensive cross linking in moulds and become infusible. Once they get set, they cannot be reshaped and reused.

18 Glucose and galactose are having identical configuration in all the positions except position.

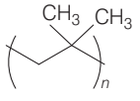
(a) C-3 (b) C-4 (c) C-2 (d) C-5

Ans. ***(b)***

Glucose and galactose are having identical configuration at all the positions except at C-4 position. Both of them are diastereomers that differ in configuration at only one chirality center. Hence, these are called epimers. Structures of glucose and galactose are as follows:



19 The correct name of the following polymer is



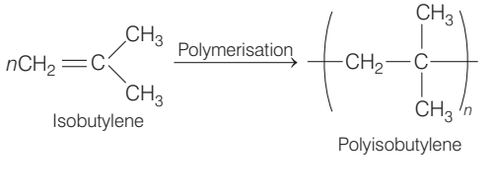
[2019, 12 April Shift-I]

(a) polyisobutane (b) polytert-butylene
(c) polyisoprene (d) polyisobutylene

Ans. ***(d)***

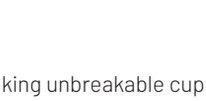
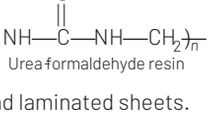
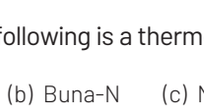
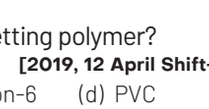
The correct name of the given polymer is polyisobutylene. It's monomer unit is isobutylene.

Reaction involved is as follows :



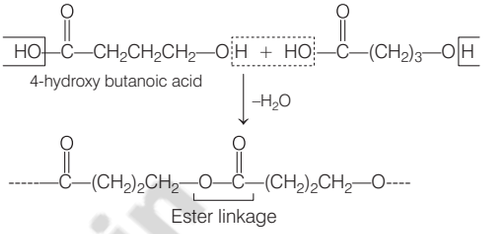
The above reaction proceed *via* addition polymerisation. Polymer is formed by the repeated addition of monomer molecules possessing double bond.

20 The homopolymer formed from 4-hydroxybutanoic acid is
[2019, 11 Jan Shift-II]

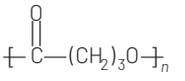
(a) 
(b) 
(c) 
(d) 

Ans. ***(c)***

On polymerisation, 4-hydroxy butanoic acid will produce a condensation homopolymer by loss of H_2O molecules.



The homopolymer obtained can also be represented as



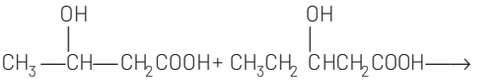
21 Poly-β-hydroxybutyrate-Co-β-hydroxyvalerate (PHBV) is a copolymer of .....

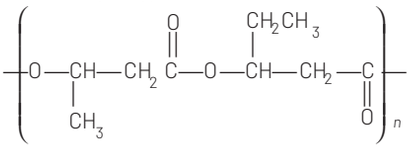
(a) 3-hydroxybutanoic acid and 2-hydroxypentanoic acid
(b) 2-hydroxybutanoic acid and 3-hydroxypentanoic acid
(c) 3-hydroxybutanoic acid and 4-hydroxypentanoic acid
(d) 3-hydroxybutanoic acid and 3-hydroxypentanoic acid

[2019, 12 Jan Shift-I]

Ans. ***(d)***

Poly-β-hydroxy butyrate Co-β-hydroxyvalerate (PHBV) is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. It is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment. The reaction involved is as follows :





22 Which of the following statements about low density polythene is false? **[JEE Main 2016]**

(a) It is a poor conductor of electricity
(b) Its synthesis required dioxygen or a peroxide initiator as a catalyst
(c) It is used in the manufacture of buckets, dustbins etc.
(d) Its synthesis requires high pressure

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Ans. *(c)*

High density polythene is used in the manufacture of buckets, dustbins etc.

23 Which polymer is used in the manufacture of paints and lacquers? **[JEE Main 2015]**

(a) Bakelite (b) Glyptal
(c) Polypropene (d) Polyvinyl chloride

Ans. *(b)*

(a) Bakelite is used for making gears, protective coating and electrical fittings.
(b) Glyptal is used in the manufacture of paints and lacquers.
(c) PP is used in the manufacture of textile, packaging materials etc.
(d) Polyvinyl chloride (PVC) is used in the manufacture of rain coats, hand bags, leather clothes etc.

24 The polymer containing strong intermolecular forces *e.g.*, hydrogen bonding, is **[AIEEE 2010]**

(a) teflon (b) nylon 6 6
(c) polystyrene (d) natural rubber

Ans. *(b)*

Nylon-6 6 contains strong intermolecular forces like hydrogen bonds that are formed between $-\overset{\overset{O}{\|}}{C}-NH-$ group of successive chains.

25 Buna-N synthetic rubber is a copolymer of **[AIEEE 2009]**

(a) $H_2C=CH-\overset{\overset{Cl}{|}}{C}=CH_2$ and $H_2C=CH-CH=CH_2$
(b) $H_2C=CH-CH=CH_2$ and $H_5C_6-CH=CH_2$
(c) $H_2C=CH-CN$ and $H_2C=CH-CH=CH_2$
(d) $H_2C=CH-CN$ and $H_2C-\overset{\overset{CH_3}{|}}{C}=CH_2$

Ans. *(c)*

Buna-N is actually abbreviated form, where Bu represents 1,3-butadiene, na represents Na, sodium and N represents nitrile (acrylonitrile).

Thus, buna-N is a copolymer of 1,3-butadiene and acrylonitrile usually polymerise in the presence of sodium.

26 Which of the following is fully fluorinated polymer? **[AIEEE 2005]**

(a) PVC (b) Thiokol
(c) Teflon (d) Neoprene

Ans. *(c)*

Teflon is $+CF_2-CF_2+_n$.

27 Which of the following is a polyamide?

(a) Bakelite (b) Terylene
(c) Nylon-6 6 (d) Teflon **[AIEEE 2005]**

Ans. *(c)*

Nylon-6 6 is a polyamide of hexamethylene diamine $(CH_2)_6(NH_2)_2$ and adipic acid $(CH_2)_4(COOH)_2$.

(Each reactant has six-carbon chain, hence trade code 6, 6 is used.)

28 Nylon threads are made up of **[AIEEE 2003]**

(a) polyvinyl polymer (b) polyester polymer
(c) polyamide polymer (d) polyethylene polymer

Ans. *(c)*

Nylon threads are made up of polyamide, some common are

Nylon 6 : $H_2N-(CH_2)_5-\overset{\overset{O}{\|}}{C}-OH$; Monomer Polymer

$$-HN-(CH_2)_5-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_5-\overset{\overset{O}{\|}}{C}-NH-$$

Nylon 6 6 : $HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-COOH$

and $H_2N-(CH_2)_6-NH_2$; Copolymer

$$+\left[\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH\right]+$$

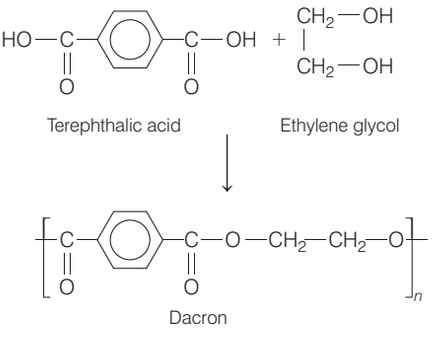
TOPIC 2
Methods of Polymerisation

29 Monomer units of dacron polymer are **[2021, 01 Sep Shift-II]**

(a) ethylene glycol and phthalic acid
(b) ethylene glycol and terephthalic acid
(c) glycerol and terephthalic acid
(d) glycerol and phthalic acid

Ans. *(b)*

Monomer units of dacron are ethylene glycol and terephthalic acid.



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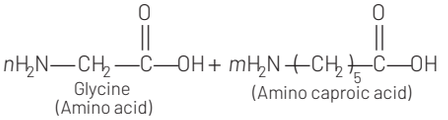
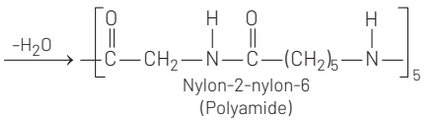
30 A biodegradable polyamide can be made from **[2021, 25 July Shift-II]**

(a) glycine and isoprene
(b) hexamethylene diamine and adipic acid
(c) glycine and aminocaproic acid
(d) styrene and caproic acid

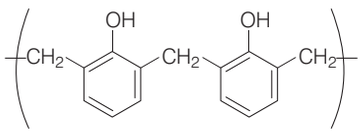
Ans. ***(c)***

A biodegradable polyamide nylon-2-nylon-6 is made from glycine and amino caproic acid.





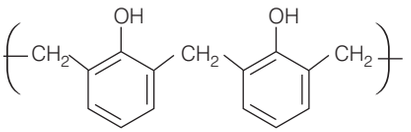
Here; is amide linkage.

31 

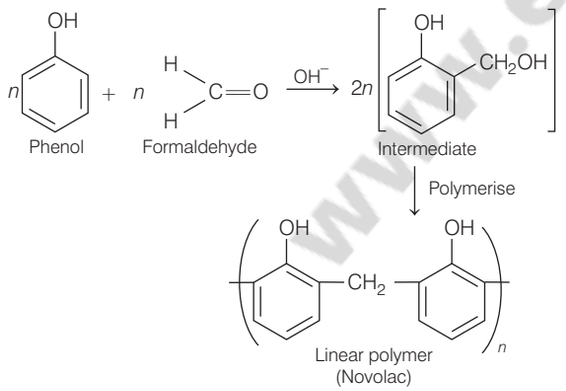
is a repeating unit for **[2021, 25 July Shift-I]**

(a) novolac (b) buna-N
(c) acrilan (d) neoprene

Ans. ***(a)***



is a repeating unit for novolac.



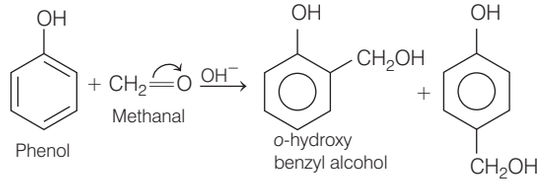
Novolac is low molecular weight polymer derived from phenol and formaldehyde. They are related to bakelite, which is more highly cross-linked.

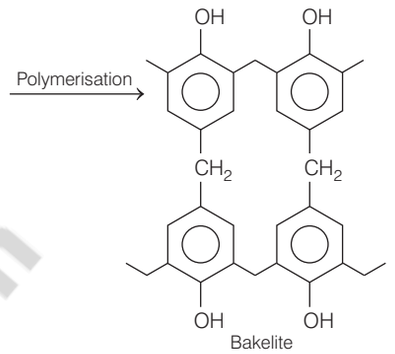
32 Bakelite is a cross-linked polymer of formaldehyde and **[2021, 20 July Shift-II]**

(a) PHBV (b) buna-S (c) novolac (d) dacron

Ans. ***(c)***

Bakelite is a cross-linked polymer of formaldehyde and novolac.





Condensation reaction between phenol and formaldehyde with excess of phenol form novolac.

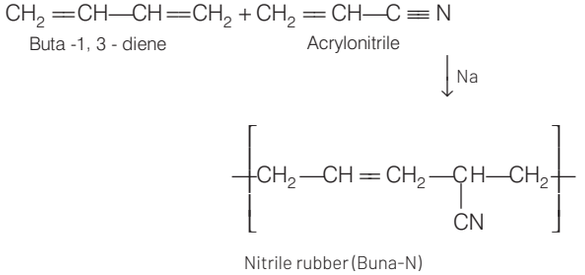
Novolac on further heating with formaldehyde undergoes cross-linking to form bakelite.

33 Which one of the following polymers is not obtained by condensation polymerisation? **[2020, 5 Sep Shift-II]**

(a) Nylon 6, 6 (b) Buna-N
(c) Bakelite (d) Nylon 6

Ans. ***(b)***

Buna-N is an addition polymer. It is obtained by copolymerisation of 1, 3-butadiene and acrylonitrile in the presence of a peroxide catalyst.



34 Preparation of bakelite proceeds *via* reactions **[2020, 8 Jan Shift-II]**

(a) Electrophilic addition and dehydration
(b) Condensation and elimination
(c) Nucleophilic addition and dehydration
(d) Electrophilic substitution and dehydration

Ans. ***(d)***

Preparation of bakelite proceeds *via* electrophilic substitution and dehydration reactions. It is shown below :

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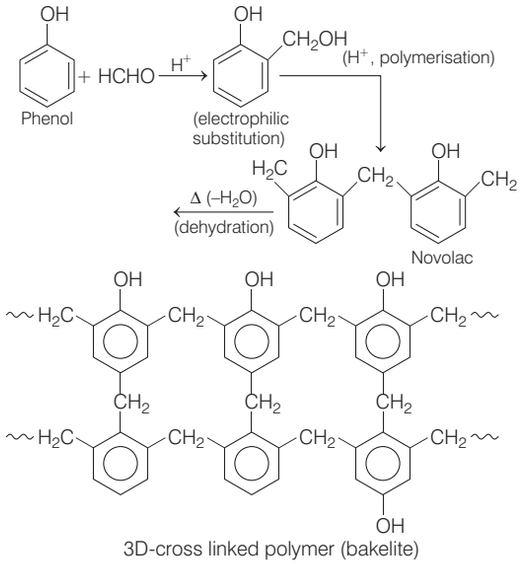


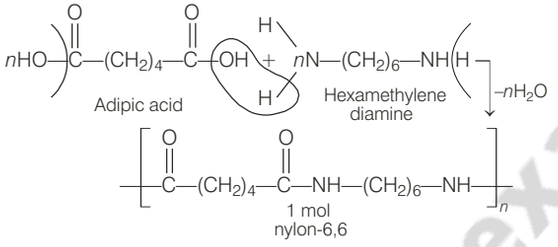
35 Which of the following is a condensation polymer?

[2019, 10 April Shift-I]

(a) Nylon-6, 6 (b) Neoprene (c) Teflon (d) Buna - S

Ans. ***(a)***

Nylon-6, 6 (an amide) is a condensation copolymer because it is obtained by condensation between adipic acid and hexamethylenediamine.



Neoprene, teflon and buna-S are addition polymers.

36 The correct match between Item-I and Item-II is

[2019, 10 April Shift-II]

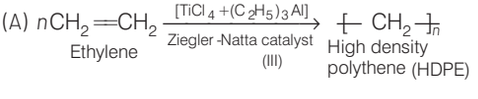
	Item-I		Item-II
A.	High density polythene	I.	Peroxide catalyst
B.	Polyacrylonitrile	II.	Condensation at high temperature and pressure
C.	Novolac	III.	Ziegler-Natta catalyst
D.	Nylon-6	IV.	Acid or base catalyst

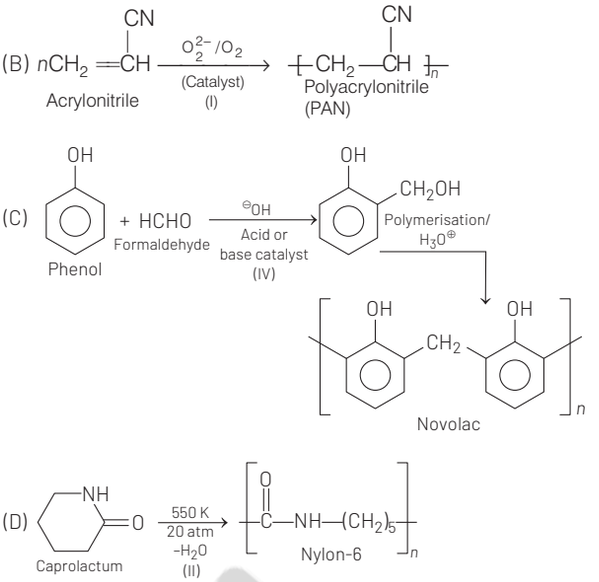
Codes

	A	B	C	D
(a)	III	I	IV	II
(c)	III	V	I	III

	A	B	C	D
(b)	IV	II	I	III
(d)	III	I	II	IV

Ans. ***(a)***

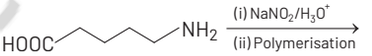


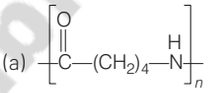


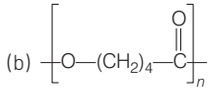
Thus, the correct match is as follows :

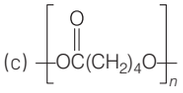
(A)→(III), (B)→(I), (C)→(IV), (D)→(II)

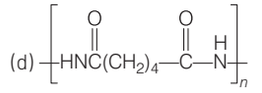
37 The polymer obtained from the following reaction is:



(a) 

(b) 

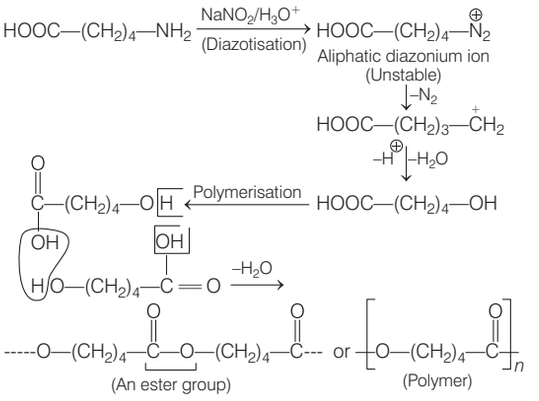
(c) 

(d) 

[2019, 11 Jan Shift-I]

Ans. ***(c)***

Given amino acid on reaction with $NaNO_2/H_3O^+$ gives diazotisation reaction which further evolves —N_2 gas along with formation of carbocation. On further reaction with water, it form HOOC—(CH_2)—OH that undergoes polymerisation to give polymer.



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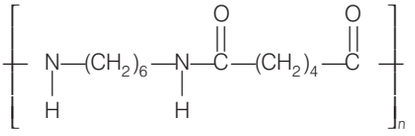
38 The two monomers for the synthesis of nylon 6, 6 are **[2019, 12 Jan Shift-II]**

(a) $HOOC(CH_2)_4COOH, H_2N(CH_2)_4NH_2$
(b) $HOOC(CH_2)_6COOH, H_2N(CH_2)_4NH_2$
(c) $HOOC(CH_2)_4COOH, H_2N(CH_2)_6NH_2$
(d) $HOOC(CH_2)_6COOH, H_2N(CH_2)_6NH_2$

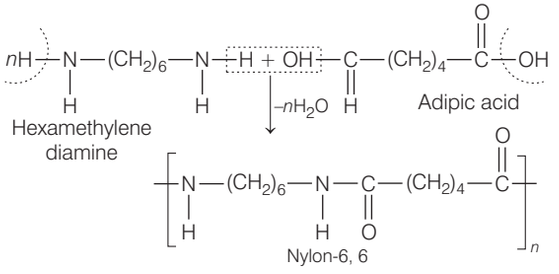
Ans. ***(c)***

Nylon 6, 6 has following structure:



6 C-atoms 6 C-atoms

As it is a condensation polymer hence, each of its monomeric unit must contain 6 carbon atoms in them. Hence, a combination of adipic acid and hexamethylene diamine is the correct answer. Both of these units react as follows to form nylon-6, 6.

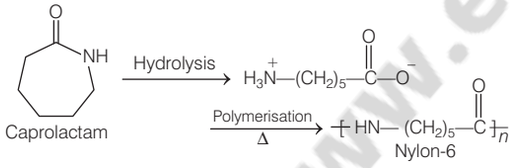


39 The formation of which of the following polymers involves hydrolysis reaction? **[JEE Main 2017]**

(a) Nylon-6 (b) Bakelite (c) Nylon-6, 6 (d) Terylene

Ans. ***(a)***

Nylon-6 or perlon is prepared by polymerisation of amino caproic acid at high temperature. Caprolactam is first hydrolysed with water to form amino acid which on heating undergoes polymerisation to give nylon-6.



40 The species which can best serve as an initiator for the cationic polymerization is **[AIEEE 2012]**

(a) $LiAlH_4$ (b) HNO_3
(c) $AlCl_3$ (d) BaLi

Ans. ***(c)***

Electron-deficient specie (Lewis acid) is used as an initiator for cationic polymerization.

41 Thermosetting polymer, bakelite is formed by the reaction of phenol with **[AIEEE 2011]**

(a) CH_3CH_2CHO (b) CH_3CHO
(c) HCHO (d) HCOOH

Ans. ***(c)***

Bakelite is a thermosetting polymer formed by the condensation reaction of phenol with HCHO in the presence of conc. H_2SO_4.

It is thus, a cross-linked polymer in which condensation takes place at *o*- and *p*–positions.

Thus, HCHO is the correct option.

42 Bakelite is obtained from phenol by reacting with **[AIEEE 2008]**

(a) $(CH_2OH)_2$ (b) CH_3CHO
(c) CH_3COCH_3 (d) HCHO

Ans. ***(d)***

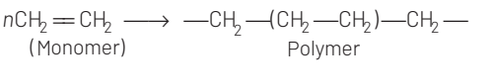
Bakelite is obtained from phenol by reacting with HCHO in the acidic or alkaline medium.

43 Monomers are converted to polymer by

(a) hydrolysis of monomers **[AIEEE 2002]**
(b) condensation reaction between monomers
(c) protonation of monomers
(d) None of the above

Ans. ***(b)***

Condensation is the process of aggregation of more than one molecule without loosing any atom or group (sometimes smaller group or atoms $H_2O, R—OH$ etc are released).



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28

Biomolecules

TOPIC 1
Carbohydrates

01 Which one of the following compounds contain β-C_1—C_4 glycosidic linkage ?

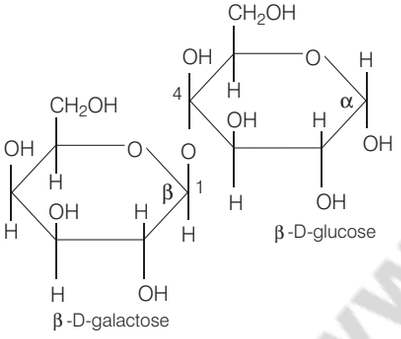
[2021, 31 Aug Shift-I]

(a) Lactose
(b) Sucrose
(c) Maltose
(d) Amylose

Ans. ***(a)***

Lactose contains β-C_1—C_4 glycosidic linkage.

The linkage is between C-1 of galactose and C-4 of glucose. It's structure is as follows :



Hence, correct option is (a).

02 Hydrolysis of sucrose gives

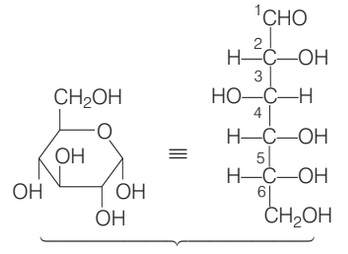
[2021, 27 Aug Shift-II]

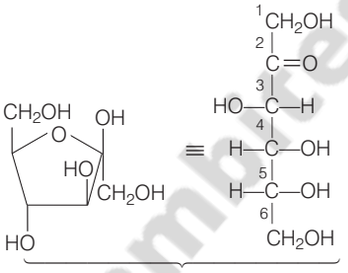
(a) α-D-(–)-glucose and β-D(–)-fructose
(b) α-D-(+)-glucose and β-D-(+)-fructose
(c) α-D-(–)-glucose and β-D-(+)-fructose
(d) α-D-(+)-glucose and β-D-(–)-fructose

Ans. ***(d)***

Hydrolysis of sucrose gives,

Sucrose + $H_2O \rightleftharpoons$ α-D-(+)-glucose + β-D-(–)-fructose





Therefore, option (d) is correct answer.

'D' represents the orientation of hydroxyl group at the chiral carbon that is farthest from the highest oxidised carbon (aldehyde group in case of glucose and keto group in fructose) when the — OH group is on the right side, 'L' is used when — OH group is on the left side. (+) and (–) represents the direction of rotation of plane polarised light (+) is clockwise rotation and (–) is anticlockwise rotation.

α-is used when —OH group at anomeric carbon is below the ring in Haworth projection, β is used when — OH group at anomeric carbon is above the rings in Haworth projection.

03 Compound *A* gives D-galactose and D-glucose on hydrolysis. The compound *A* is **[2021, 27 July Shift-II]**

(a) amylose
(b) sucrose
(c) maltose
(d) lactose

Ans. ***(d)***

Lactose is a disaccharide of β-D-galactose and β-D-glucose with C_1 of galactose and C_4 of glucose linkage. Complete reactions are as follows

(a) Amylose + $H_2O \xrightarrow{H^+}$ D-glucose

(b) Sucrose + $H_2O \xrightarrow{H^+}$ D-glucose + D-fructose

(c) Maltose + $H_2O \xrightarrow{H^+}$ D-glucose

(d) Lactose + $H_2O \xrightarrow{H^+}$ D-glucose + D-galactose

04 Given below are two statements : One is labelled as Assertion (A) and other is labelled as Reason (R).

Assertion (A) Sucrose is a disaccharide and a non-reducing sugar.

Reason (R) Sucrose involves glycosidic linkage between C_1 of β-glucose and C_2 of α-fructose.

Choose the most appropriate answer from the options given below. **[2021, 26 Aug Shift-II]**

(a) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(b) (A) is false but (R) is true.
(c) (A) is true but (R) is false.
(d) Both (A) and (R) are true and (R) is the correct explanation of (A).

Ans. ***(c)***

Assertion is true but Reason is false. Sucrose is formed by linkage of C_1 of α-D glucose and C_2 of β-D fructose. The glycosidic bond in sucrose is formed between reducing ends of both glucose and fructose.

Sucrose is a disaccharide and a non-reducing sugar as it contains no free —CHO group (Anomeric carbon of

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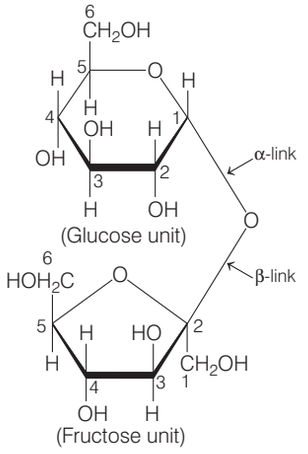
both monosaccharides are involved in formation of glycosidic bond).

The structure is as follows



05 Identify the incorrect statement from the following.

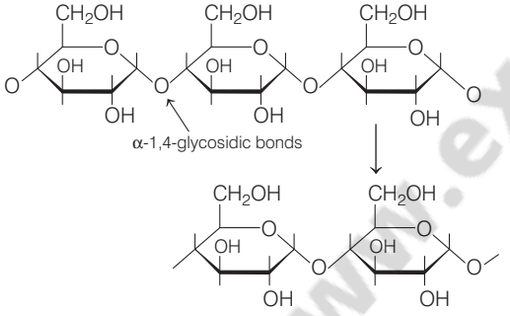
[2021, 20 July Shift-I]

(a) Amylose is a branched chain polymer of glucose.
(b) Starch is a polymer of α-D-glucose .
(c) β-glycosidic linkage makes cellulose polymer.
(d) Glycogen is called as animal starch.

Ans. ***(a)***

Amylose consists of linear, helical chains of roughly 500 to 20,000 D-glucose monomers linked together through α -1,4 glycosidic bonds. In contrast to amylose, amylopectin is branched.

Linear structure of amylose is as follows



Therefore, option (a) is incorrect statement.

06 Which one among the following chemical tests is used to distinguish monosaccharide from disaccharide ?

[2021, 27 July Shift-I]

(a) Seliwanoff's test (b) Iodine test
(c) Barfoed test (d) Tollen's test

Ans. ***(c)***

A monosaccharide is a single sugar molecule like glucose, fructose, galactose while disaccharides are double sugars, e.g. sucrose.

(c) Barfoed's test is used for distinguishing monosaccharides from reducing disaccharides. Monosaccharides usually react in about 1-2 minutes while disaccharide take 7-12 minutes to react with reagent.

Barfoed's reagent in cupric acetate in 1% acetic acid. Brick red colour is obtained in this test due to formation of cuprous oxide.

(a) Seliwanoff's test is used to distinguish between functional group (ketone or aldehyde) present on sugar.
(b) Iodine test is used for detection of starch and help to distinguish starch from monosaccharide, disaccharides and polysaccharides.
(d) While Tollen's test is used to determine the presence of an aldehyde or ketone group in unknown solution.

07 A non-reducing sugar "*A*" hydrolyses to give two reducing monosaccharides. Sugar *A* is

[2021, 18 March Shift-I]

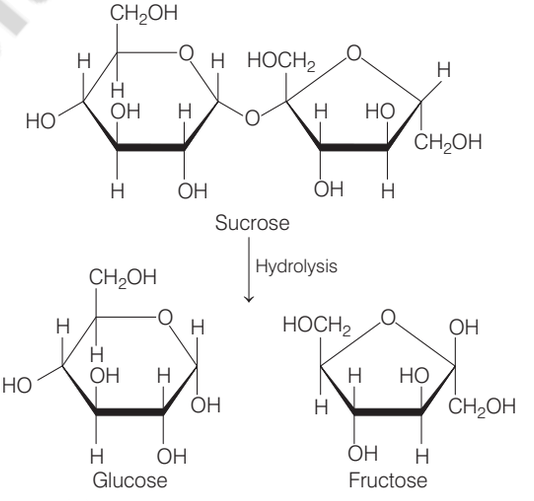
(a) fructose (b) galactose
(c) glucose (d) sucrose

Ans. ***(d)***

A non-reducing sugar is one kind of carbohydrate that is not oxidised by a weak oxidising agent (an oxidising agent that oxidises aldehydes but not alcohols, such as the Tollen's reagent) in a basic aqueous solution.

$$\underset{\substack{\text{Sucrose}\\(A)\\(\text{Non-reducing}\\\text{sugar})}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-fructose}}{C_6H_{12}O_6}$$

While all others, i.e. glucose, fructose and galactose are reducing sugar.



Thus, sugar (*A*) is sucrose.

08 $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Enzyme } A} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Enzyme } B} 2\underset{\text{Ethanol}}{C_2H_5OH} + 2CO_2$

In the above reactions, the enzyme *A* and enzyme *B* respectively are

[2021, 17 March Shift-II]

(a) amylase and invertase
(b) invertase and amylase
(d) invertase and zymase
(d) zymase and invertase

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Ans. ***(c)***

Invertase and zymase are enzyme *A* and enzyme *B* respectively.

Invertase is the enzyme that catalyses the hydrolysis of sucrose with a resulting mixture of fructose and glucose, which is called inverted sugar. It cleaves the O—C bond.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Zymase is an enzyme that catalyses the fermentation of sugar into ethanol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

09 Fructose is an example of **[2021, 17 March Shift-II]**

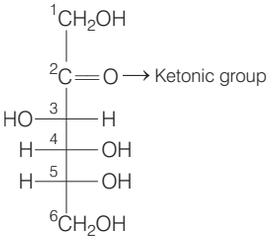
(a) pyranose (b) ketohexose
(c) aldohexose (d) heptose

Ans. ***(b)***

Fructose is an example of ketohexose is a class of sugars that contains six-carbon atoms and a ketonic group. Fructose has a ketonic group with six carbon atoms.

It contains five hydroxyl group and one ketonic group.

The structure of fructose is



10 Match List-I with List-II.

	List-I		List-II
A.	Sucrose	(i)	β-D-galactose and β-D-glucose
B.	Lactose	(ii)	α-D-glucose and β-D-fructose
C.	Maltose	(iii)	α-D-glucose and α-D-glucose

Choose the correct answer from the options given below. **[2021, 26 Feb Shift-II]**

(a) A → (i), B → (iii), C → (ii)
(b) A → (iii), B → (i), C → (iii)
(c) A → (ii), B → (i), C → (iii)
(d) A → (iii), B → (ii), C → (i)

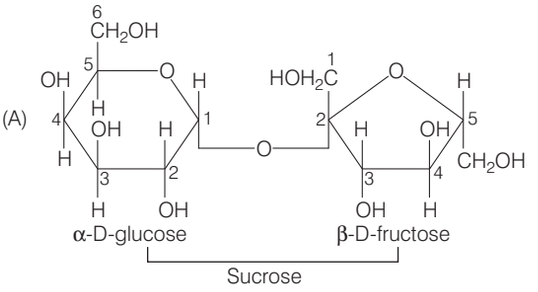
Ans. ***(c)***

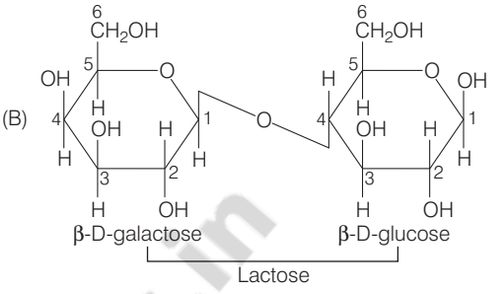
Sucrose (cane sugar), lactose (milk sugar) and maltose are disaccharides in which two monosaccharides are hold together by a glycosidic linkage.

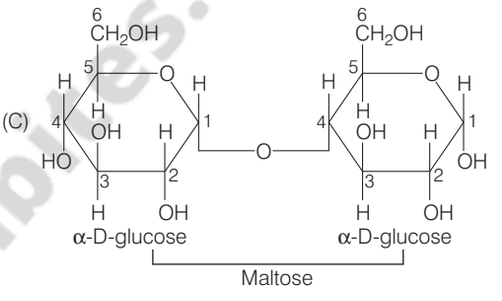
(A) In sucrose, C_1 of α - D - glucose and C_2 of β-D-fructose are linked together (ii).

(B) In lactose, C_1 of β - D-galactose and C_4 of β-D-glucose are linked together (i).

(C) In maltose, C_1 of α - D-glucose is linked to C_4 of another α - D - glucose unit (iii).

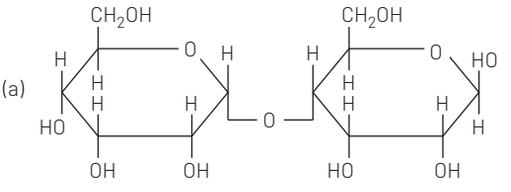


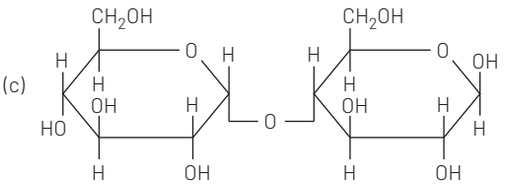


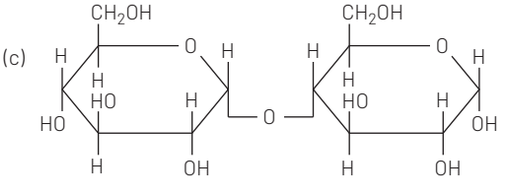


So, option (c) is the correct answer.

11 Which of the following is correct structure of α-anomer of maltose? **[2021, 25 Feb Shift-II]**







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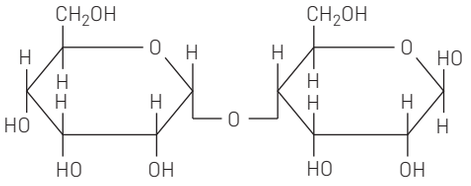
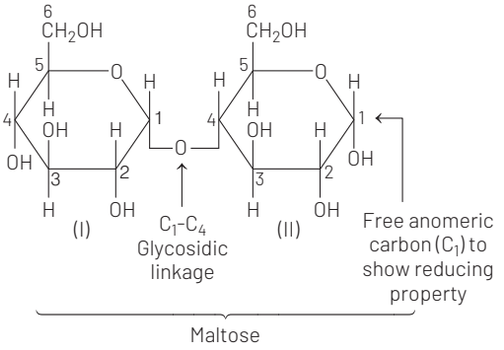
(d)



Ans. ***(c)***

Maltose is a disaccharide which is made of two α-D-glucose units in which C_1 (anomeric carbon) of one glucose (I) is linked to C_4 of another glucose unit (II).

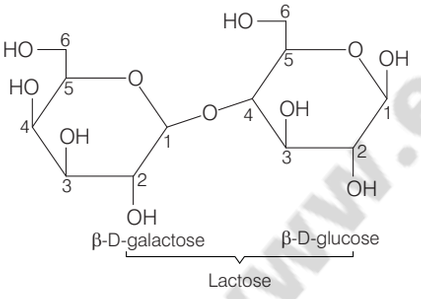


12 Which of the glycosidic linkage between galactose and glucose is present in lactose? **[2021, 25 Feb Shift-I]**

(a) C-1 of galactose and C-4 of glucose
(b) C-1 of galactose and C-6 of glucose
(c) C-1 of glucose and C-4 of galactose
(d) C-1 of glucose and C-6 of galactose

Ans. ***(a)***

Glycosidic linkage is a type of covalent bond that joins carbohydrate molecules to another group.



In lactose, glycosidic linkage is formed between C-1 of galactose and C-4, glycosidic of glucose.

13 Consider the following reactions :

(i) Glucose + $ROH \xrightarrow{\text{Dry HCl}}$ Acetal $\xrightarrow[(CH_3CO)_2O]{x \text{ eq. of}}$ Acetyl derivative

(ii) Glucose $\xrightarrow{Ni/H_2} A \xrightarrow[(CH_3CO)_2O]{y \text{ eq.of}}$ Acetyl derivative

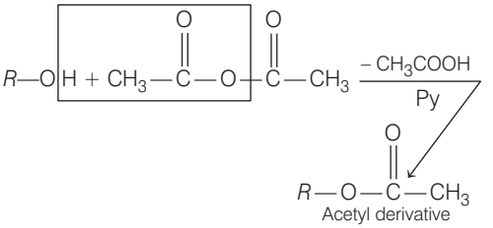
(iii) Glucose $\xrightarrow[(CH_3CO)_2O]{z \text{ eq.of}}$ Acetyl derivative

'x', 'y' and 'z' in these reactions are respectively **[2020, 2 Sep Shift-I]**

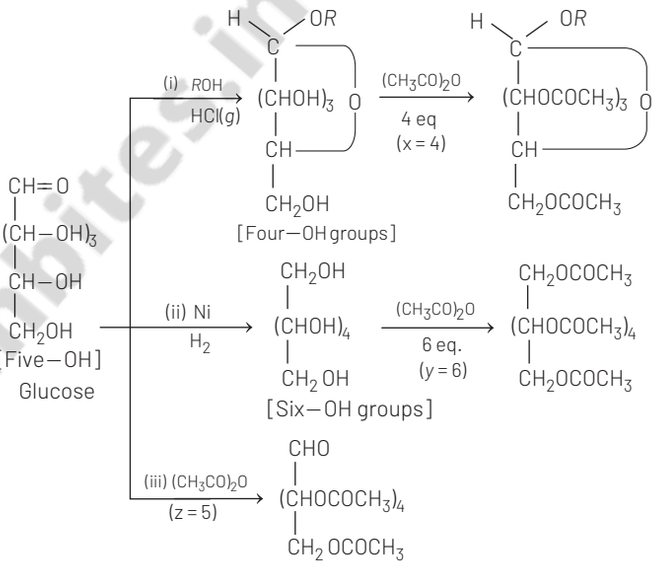
(a) 5, 4 and 5 (b) 4, 5 and 5
(c) 5, 6 and 5 (d) 4, 6 and 5

Ans. ***(d)***

Glucose is a polyhydroxy aldohexose. Its number of free —OH groups can be calculated by acetylation process which is done by using $(CH_3CO)_2O$/Py or CH_3COCl/Py as :



Or $R(OH)_n + n(CH_3CO)_2O \xrightarrow[Py]{-nCH_3COOH} R(OCOCH_3)_n$



So, *x*, *y* and *z* in these reactions are 4, 6 and 5 respectively.

14 The correct observation in the following reactions, is

Sucrose $\xrightarrow[\text{Cleavage (Hydrolysis)}]{\text{Glycosidic bond}} A + B \xrightarrow[\text{reagent}]{\text{Seliwanoff's}}$

[2020, 2 Sep Shift-II]

(a) Formation of blue colour
(b) Gives no colour
(c) Formation of red colour
(d) Formation of violet colour

Ans. ***(c)***

$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Cleavage (Mutarotation)}]{\text{Glycosidic bond}} \underset{\substack{\text{Glucose}\\ A \text{ (Say)}}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ B}}{C_6H_{12}O_6}$

$\xrightarrow[\text{Dilute resorsinol + Dilute HCl}]{\text{Soliwanoffs reagent}}$ Red colouration

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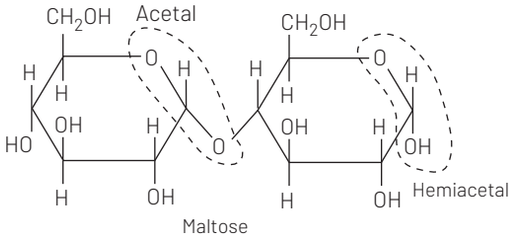
Soliwanoff's reagent test is given by ketohexoses (here, *B*) and sucrose only but not by any aldohexose (here, *A*), lactose and maltose.

15 What are the functional groups present in the structure of maltose? **[2020, 4 Sep Shift-I]**

(a) One ketal and one hemiketal
(b) One acetal and one ketal
(c) One acetal and one hemiacetal
(d) Two acetals

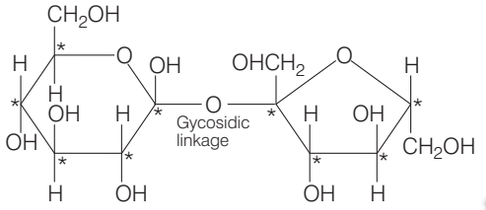
Ans. ***(c)***

The functional groups present in the structure of maltose is one acetal and one hemiacetal. It is illustrated in following structure.



16 The number of chiral carbons present in sucrose is ..... . **[2020, 5 Sep Shift-II]**

Ans. ***(9.00)***



Total number of chiral carbon in sucrose = 9

17 Which one of the following statements is not true? **[2020, 6 Sep Shift-II]**

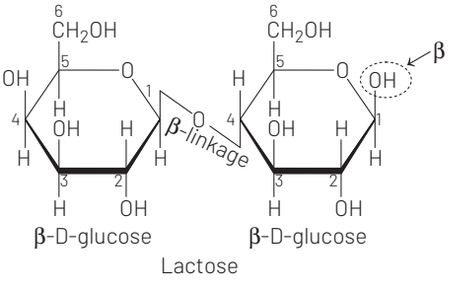
(a) Lactose contains α-glycosidic linkage between C_1 of galactose and C_4 of glucose.
(b) Lactose is a reducing sugar and it gives Fehling's test.
(c) Lactose ($C_{11}H_{22}O_{11}$) is a disaccharide and it contains 8 hydroxyl groups.
(d) On acid hydrolysis, lactose gives one molecule of D(+) - glucose and one molecule of D (+) - galactose

Ans. ***(a)***

Lactose contains β-glycosidic linkage between C_1 of galactose and C_4 of glucose. It is found in milk and is also known as milk sugar. On hydrolysis with dilute acid, it yield an equimolar mixture of D-glucose and D-galactose. It is a reducing sugar and gets hydrolysed by emulsion, which is an enzyme that specifically hydrolysis β-glycosidic linkages. Lactose contain anomeric —OH. So, it give Fehling test.

Now, in ΔSPT,

$$\frac{PT}{SP} = \sin 60° \Rightarrow PT = \frac{\sqrt{3}}{2}\text{ km}$$



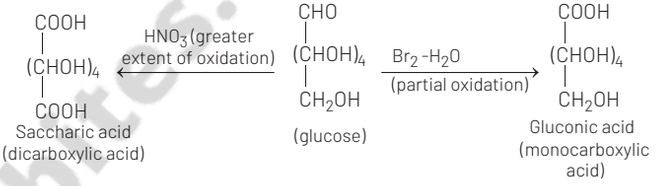
Hence, option (a) is not true.

18 Which of the following statements is correct? **[2020, 7 Jan Shift-II]**

(a) Gluconic acid is obtained by oxidation of glucose with HNO_3
(b) Gluconic acid is a dicarboxylic acid
(c) Gluconic acid can form cyclic (acetal/hemiacetal) structure
(d) Gluconic acid is a partial oxidation product of glucose

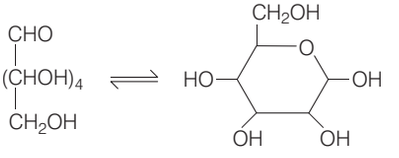
Ans. ***(d)***

The correct chemical equations are given as follows :



Therefore,

(i) Saccharic acid not gluconic acid is obtained by the oxidation of glucose with HNO_3. Thus, it is incorrect statement.
(ii) Gluconic acid is a monocarboxylic acid and not a dicarboxylic acid. Thus, it is incorrect statement.
(iii) Glucose exists predominantly in the cyclic structure than the open chain structure :



But gluconic acid can not exist in cyclic structure. (Stereochemical configurations are not specified in the structures given above, for simplicity). Thus, (iii) is incorrect.

(iv) Gluconic acid is a partial oxidation product of glucose. Hence, it is correct statement.

19 Which of the following statement is not true for glucose? **[2020, 8 Jan Shift-I]**

(a) The pentaacetate of glucose does not react with hydroxylamine to give oxime
(b) Glucose exists in two crystalline forms α and β
(c) Glucose gives Schiff's test for aldehyde
(d) Glucose reacts with hydroxylamine to form oxime

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Ans. ***(c)***

The incorrect statement is (c). It can be corrected as follows : Glucose does not give Schiff's test due to absence of free —CHO in cyclic form.

The correct statements can be explained as follows :

(a) Pentaacetate of glucose does not react with hydroxylamine to give oxime. Because, the cyclic form (pyranose) of glucose after pentaacetate formation does not have free —CHO or $\rangle C{=}O$ group.

(b) Cyclic form of glucose has two diastereomeric forms which are named as α and β form. Each form its own crystal.

(d) Glucose reacts with hydroxylamine to form oxime.

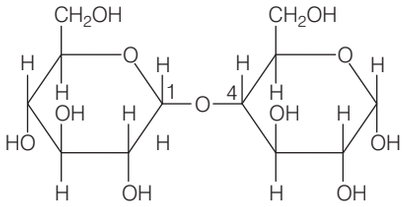
20 Two monomers in maltose are **[2020, 8 Jan Shift-II]**

(a) α-D-glucose and α-D-glucose
(b) α-D-glucose and α-D-galactose
(c) α-D-glucose and β-D-glucose
(d) α-D-glucose and α-D-fructose

Ans. ***(a)***

Maltose is a disaccharide formed from monosaccharides α-D-glucose and α-D glucose *via* C_1—C_4 glycosidic linkage.

It is shown in following structure:

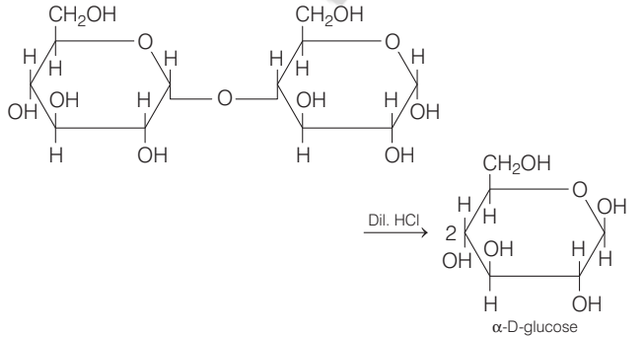


21 Maltose on treatment with dilute HCl gives **[2019, 8 April Shift-I]**

(a) D-glucose and D-fructose (b) D-fructose
(c) D-galactose (d) D-glucose

Ans. ***(d)***

Maltose on treatment with dil. HCl gives D-glucose. Hydrolysis of maltose yields two moles of α- D-glucose. Thus, it is composed of two α-D-glucose units in which C-1 of one glucose unit (I) is linked to C-4 of another glucose unit (II). The free aldehyde group can be produced at C-1 of second glucose in solution and it shows reducing properties. So, it is a reducing sugar.



22 Fructose and glucose can be distinguished by **[2019, 8 April Shift-II]**

(a) Fehling's test (b) Barfoed's test
(c) Benedict's test (d) Seliwanoff's test

Ans. ***(d)***

Both fructose and glucose give following test positive.

(i) Fehling's test (red ppt. of Cu_2O is obtained).
(ii) Barfoed's test (red ppt. of Cu_2O is obtained)
(iii) Benedict's test (red ppt. of Cu_2O is obtained)

Fehling's solution : $CuSO_4$ + Na, K-tartrate (Rochelle salt)

Barfoed's reagent $\underset{(7\%)}{(CH_3COO)_2Cu} + \underset{(1\%)}{CH_3COOH} + \underset{(92\%)}{H_2O}$

Benedict's solution : $CuSO_4$ + Na-citrate + Na_2CO_3

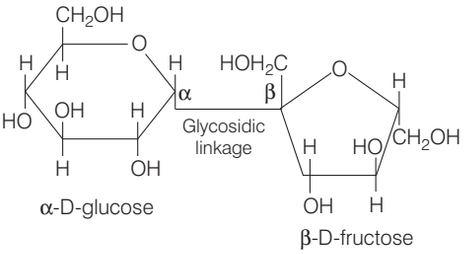
Seliwanoff's test is used to differentiate between ketose and aldose. The reagent is a solution of resorcinol in concentrated HCl. The reagent when heated along with a sugar will produce furfural or hydroxy-methylfurfural, which further reacts to give red color. Ketose (fructose) reacts more quickly than aldose (glucose).

23 Which of the following statement is not true about sucrose? **[2019, 9 April Shift-I]**

(a) It is also named as invert sugar.
(b) The glycosidic linkage is present between C_1 of α-glucose and C_2 of β-fructose
(c) It is a non-reducing sugar
(d) On hydrolysis, it produces glucose and fructose

Ans. ***(b)***

Statement-(b) is not true for sucrose. It is linked through a glycosidic linkage between C-1 of α-glucose and C-2 of β-fructose. Since, the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.



On hydrolysis with acids or enzyme, sucrose gives equimolar mixture of D-(+)-glucose and D-(–)-fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{HCl} \underset{\text{D-(+)-glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-fructose}}{C_6H_{12}O_6}$$

24 Amylopectin is composed of **[2019, 10 April Shift-I]**

(a) β-D-glucose, C_1-C_4 and C_2-C_6 linkages
(b) α-D-glucose, C_1-C_4 and C_2-C_6 linkages
(c) β-D-glucose, C_1-C_4 and C_1-C_6 linkages
(d) α-D-glucose, C_1-C_4 and C_1-C_6 linkages

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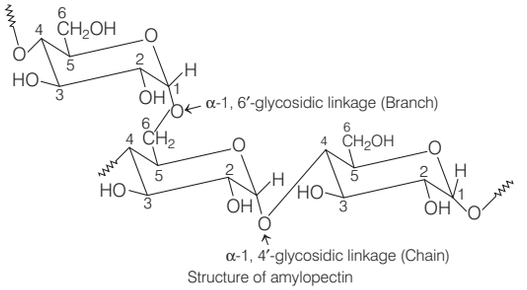
Ans. ***(d)***

Amylopectin is the water-soluble component of starch. It is a branched-chain polymer of α-D-glucose. The main chain consists of an α – 1, 4′- glycosidic linkages between α-D- glucose units and the branches are connected to the main chain by α - 1,6′- glycosidic linkages. Its structure can be represented as:



Structure of amylopectin

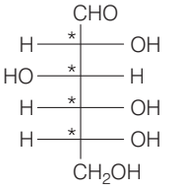
25 Number of stereo-centers present in linear and cyclic structures of glucose are respectively **[2019, 10 April Shift-II]**

(a) 4 and 5 (b) 4 and 4
(c) 5 and 4 (d) 5 and 5

Ans. ***(a)***

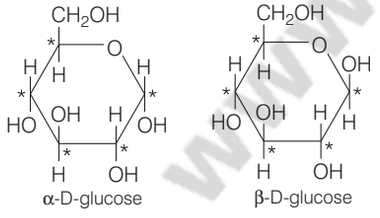
Key Idea Chiral centre is also called stereo-centre or stereogenic center.

Linear structure of glucose is as follows :



Fischer formula
Number of stereo-centre (C^*) = 4.

Cyclic structure of glucose are as follows :


α-D-glucose β-D-glucose

Haworth formula Number of stereo-centre (C^*) in each anomer = 5.

26 Which of the given statements is incorrect about glycogen? **[2019, 12 April Shift-II]**

(a) It is straight chain polymer similar to amylose
(b) Only α-linkages are present in the molecule
(c) It is present in animal cells
(d) It is present in some yeast and fungi

Ans. ***(a)***

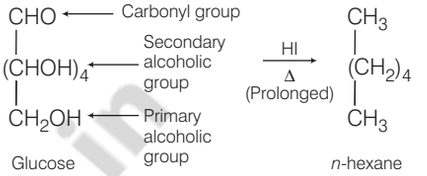
Statement (a) is incorrect. Glycogen is not a straight chain polymer similar to amylose. It is highly branched structure similar to amylopectin. It is known to be the storage material of animals. It is found in liver, muscles and brain. It breaks down to glucose by the action of enzymes when body needs a glucose. It is also found in yeast and fungi.

27 Glucose on prolonged heating with HI gives

(a) *n*-hexane (b) 1-hexene **[JEE Main 2018]**
(c) Hexanoic acid (d) 6-iodohexanal

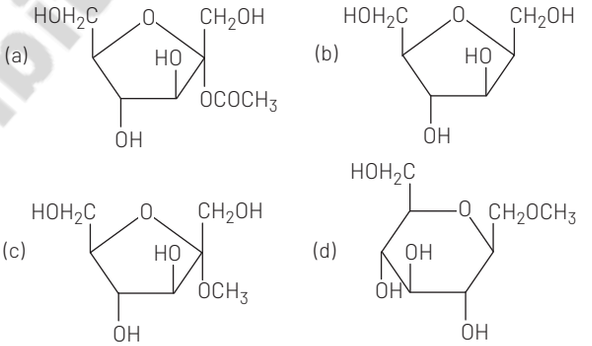
Ans. ***(a)***

HI is a strong reducing agent. It reduces both primary and secondary alcoholic groups of glucose along with the carbonyl group to produce *n*-hexane as



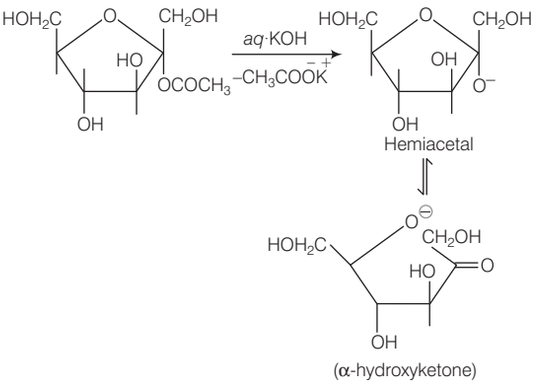
Glucose *n*-hexane

28 Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution? **[JEE Main 2017]**



Ans. ***(a)***

Sugars that have an aldehyde, a ketone, a hemiacetal or a hemiketal group is able to reduce an oxidising agent. These sugars are classified as reducing sugars.



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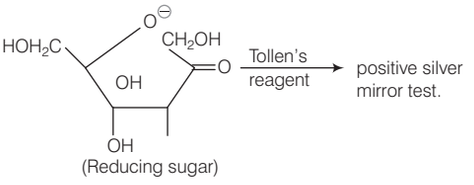
Hemiacetal can be easily reduced by oxidising agent such as Tollen's reagent.



(Reducing sugar)

29 Synthesis of each molecule of glucose in photosynthesis involves **[JEE Main 2013]**

(a) 18 molecules of ATP
(b) 10 molecules of ATP
(c) 8 molecules of ATP
(d) 6 molecules of ATP

Ans. ***(a)***

$6CO_2 + 12NADPH + 18ATP \longrightarrow C_6H_{12}O_6 + 12NADP + 18\ ADP$

30 Which of the following compounds can be detected by Molisch's test? **[AIEEE 2012]**

(a) Nitro compounds (b) Sugars
(c) Amines (d) Primary alcohols

Ans. ***(b)***

Molisch's test is used for the detection of carbohydrates. Add two drops of alcoholic solution of α-naphthol to the carbohydrate solution under study. Add conc. H_2SO_4 slowly by the side of the test tube. A violet ring is formed at the junction of the two liquids, if carbohydrate is present.

31 The change in the optical rotation of freshly prepared solution of glucose is known as **[AIEEE 2011]**

(a) tautomerism (b) racemization
(c) specific rotation (d) mutarotation

Ans. ***(d)***

A spontaneous change in the specific rotation of a solution of an optically active compound is called mutarotation.

Hemiacetal forms of α- and β-D- glucose are stable in solid state but in aqueous solution, there is opening of the cyclic structure which gives solution of constant specific rotation.

32 The two functional groups present in a typical carbohydrate are **[AIEEE 2009]**

(a) —OH and —COOH (b) —CHO and —COOH
(c) C = O and —OH (d) —OH and —CHO

Ans. ***(c, d)***

Carbohydrates are optically active polyhydroxy aldehyde or polyhydroxy ketones.

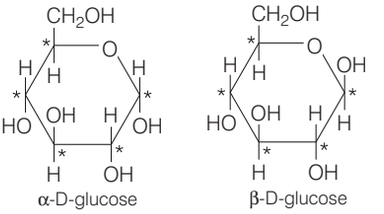
—C = O, —OH are the functional groups of typical ketose while —CH=O, OH are the functional groups of typical aldose.

33 α-D(+)-glucose and β-D-(+)-glucose are **[AIEEE 2008]**

(a) conformers (b) epimers
(c) anomers (d) enantiomers

Ans. ***(c)***

α-D(+) glucose and β-D(+) glucose are anomers of glucose.



34 The term anomers of glucose refers to

(a) isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4
(b) a mixture of (D)-glucose and (L)-glucose
(c) enantiomers of glucose
(d) isomers of glucose that differ in configuration at carbon one (C – 1) **[AIEEE 2006]**

Ans. ***(d)***

Anomers of glucose are cyclic diastereomers (epimers) differing in configuration of the hydroxyl group at C-1, existing in two forms α and β, respectively.

35 Complete hydrolysis of cellulose gives **[AIEEE 2003]**

(a) D-fructose (b) D-ribose (c) D-glucose (d) L-glucose

Ans. ***(c)***

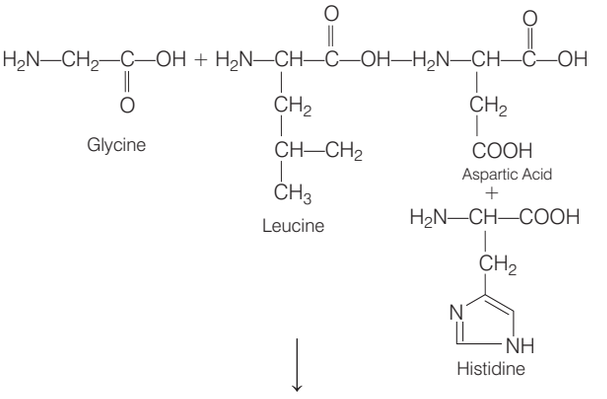
Partial hydrolysis of cellulose gives the disaccharide cellobiose ($C_{12}H_{22}O_{11}$). Cellobiose resembles maltose (which on acid catalysed hydrolysis yields two molar equivalents of D-Glucose) in every respect except one : the configuration of its glycosidic linkage.

TOPIC 2
Proteins and Enzymes

36 A peptide synthesised by the reactions of one molecule each of glycine, leucine, aspartic acid and histidine will have ..... peptide linkages. **[2021, 01 Sep Shift-II]**

Ans. ***(3)***

Peptide synthesised by reaction of glycine, leucine, aspartic acid and histidine is as follows.



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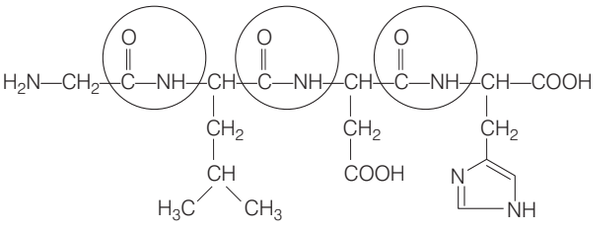


3 peptide linkage are present.

Hence, answer is 3.

37 Which of the following is not an example of fibrous protein ? **[2021, 31 Aug Shift-II]**

(a) Keratin (b) Albumin
(c) Collagen (d) Myosin

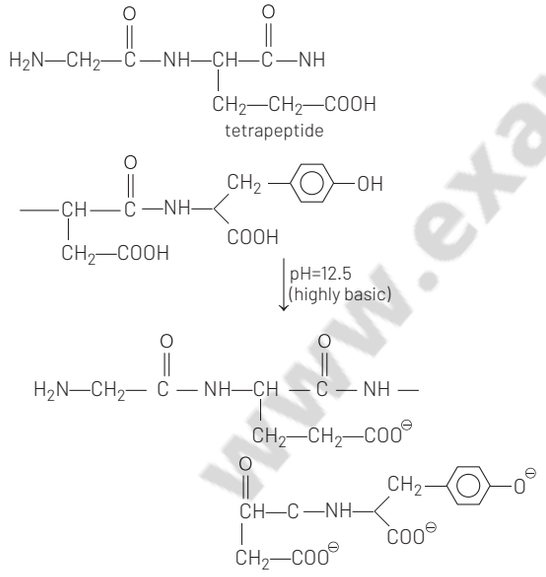
Ans. ***(b)***

Insulin and albumin are globular protein. Fibrous proteins are generally composed of long and narrow strands and have structural role while globular proteins generally have more compact and rounded shape and involved in metabolic functions.

38 The total number of negative charge in the tetrapeptide, Gly-Glu-Asp-Tyr, at pH 12.5 will be ..... . (Integer answer) **[2021, 26 Aug Shift-I]**

Ans. ***(4)***

The structures of tetrapeptide Gly-Glu-Asp-Tyr is as follows



(All protons (H^+) from carboxylic group and phenol are lost neutralised in basic medium)

Total negative charge = 4.

39 The water soluble protein is **[2021, 22 July Shift-I]**

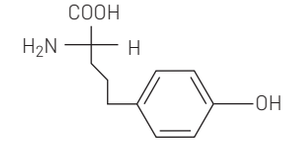
(a) fibrin
(b) albumin
(c) myosin
(d) collagen

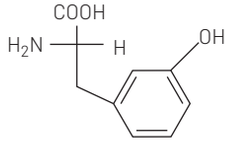
Ans. ***(b)***

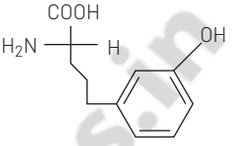
Albumin, a globular protein is soluble in water. It is half saturated with a salt such as ammonium sulphate. Serum albumin is a component of blood serum.

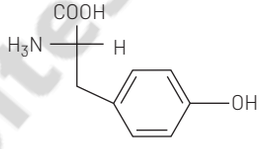
Rest all others are fibrin, collagen and myosin are insoluble in water and all are fibrous proteins.

40 Which of the following is correct structure of tyrosine? **[2021, 17 March Shift-I]**

(a) 

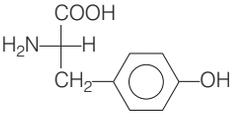
(b) 

(c) 

(d) 

Ans. ***(d)***

The structure of tyrosine amino acid is



It is an example of non-essential amino acid which contains aromatic (phenolic) ring.

41 The secondary structure of protein is stabilised by **[2021, 16 March Shift-II]**

(a) peptide bond (b) glycosidic bond
(c) hydrogen bonding (d) van der Waals' forces

Ans. ***(c)***

In secondary structure of protein, hydrogen bond is formed between and —NH— groups of the peptide bond.

Peptide linkage is an amide formed between —COOH group and $—NH_2$ group while connecting two amino acids.

The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule is called glycosidic linkage.

42 Out of the following, which type of interaction is responsible for the stabilisation of α-helix structure of proteins ? **[2021, 24 Feb Shift-I]**

(a) van der Waals' forces (b) Covalent bonding
(c) Ionic bonding (d) Hydrogen bonding

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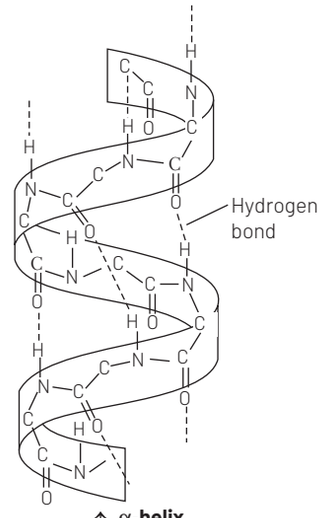
Ans. *(d)*

α-helix structure of proteins is stabilised by H-bonds between hydrogen of —NH and oxygen of —C═O group is amino acids.

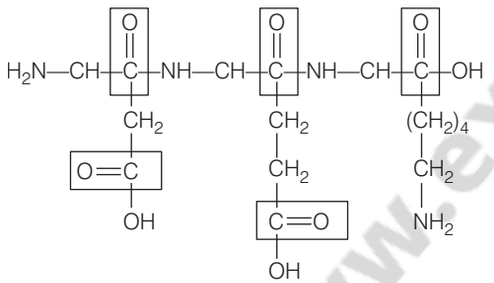


Secondary structure

43 The number of $>C=O$ groups present in a tripeptide Asp-Glu-Lys is ..... . **[2020, 3 Sep Shift-II]**

Ans. *(5)*

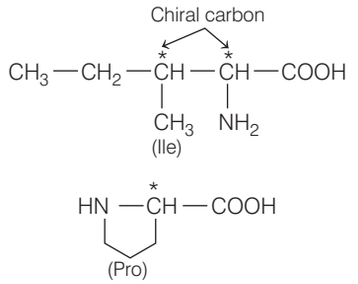
Number of $>C=O$ groups is 5 in tripeptide Asp - Glu - Lys.

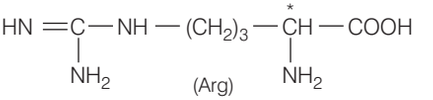


44 The number of chiral carbon(s) present in peptide, Ile-Arg-Pro, is ..... . **[2020, 5 Sep Shift-I]**

Ans. *(4)*

The amino acids present in the given tripeptide Ile-Arg-pro are isolucine, arginine and proline.





Number of chiral carbons present in the given tripeptide is 4.

45 Which of the following is not an essential amino acid? **[2020, 5 Sep Shift-I]**

(a) Leucine (b) Valine
(c) Lysine (d) Tyrosine

Ans. *(d)*

Tyrosine is not an essential amino acid and remaining all are essential amino acid.

Amino acids which are synthesised by the body, are called non-essential. On the otherhand, those amino acids which cannot be synthesised in the human body and are supplied in the form of diet are called essential amino acids the ten essential amino acids.

Valine, leucine, isoleucine, arginine lysine, threonine, methionine, phenylalanine, trpropham, histidine are essential amino acid.

46 Consider the Assertion and Reason given below.

Assertion (A) Ethene polymerised in the presence of *Ziegler-Natta* catalyst at high temperature and pressure is used to make buckets and dustbins.

Reason (R) High density polymers are closely packed and are chemically inert.

Choose the correct answer from the following: **[2020, 6 Sep Shift-I]**

(a) (A) is correct but (R) is wrong.
(b) Both (A) and (R) are correct but (R) is not the correct explanation of (A).
(c) Both (A) and (R) are correct and (R) is the correct explanation of (A).
(d) (A) and (R) both are wrong.

Ans. *(c)*

Both (A) and (R) are correct and (R) is the correct explanation of (A). High density polymers are formed by polymerisation of ethene in presence of catalyst like $(C_2H_5)_3Al + TiCl_4$ called *Ziegler- Natta* catalyst at 333 K to 343 K and under 6-7 atmospheric pressure.

High density polythene (HDP) thus produced, consists of linear molecules and has high density due to closed packing. It is used for making buckets, dustbins, bottles, pipe, etc.

Hence, the correct option is (c).

47 *A*, *B* and *C* are three biomolecules. The results of the tests performed on them are given below: **[2020 Jan Shift-II]**

	Molisch's test	Barfoed test	Biuret test
A	Positive	Negative	Negative
B	Positive	Positive	Negative
C	Negative	Negative	Positive

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A, *B* and *C* are respectively:

(a) *A* = Lactose, *B* = Glucose, *C* = Alanine
(b) *A* = Glucose, *B* = Fructose, *C* = Albumin
(c) *A* = Lactose, *B* = Glucose, *C* = Albumin
(d) *A* = Lactose, *B* = Fructose, *C* = Alanine

Ans. ***(c)***

Molisch's test is for all carbohydrates (except trioses and tetroses).

∴ Lactose, fructose and glucose give positive test.

Barfoed test is positive only for monosaccharides.

∴ It is given by glucose and fructose, not by lactose (because it is disaccharide).

Biuret test is for compounds with peptide linkages.

∴ Albumin (a protein) gives positive test. Alanine is an amino acid but have no peptide linkage.

∴ It does not give biuret test.

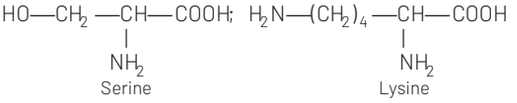
So, *A* = lactose, *B* = glucose and *C* = albumin.

48 The peptide that gives positive ceric ammonium nitrate and carbylamine tests is **[2019, 9 April Shift-II]**

(a) Lys-Asp (b) Ser-Lys (c) Gln-Asp (d) Asp-Gln

Ans. ***(b)***

The peptide that gives positive cerric ammonium nitrate and carbylamine tests is ser-lys. The structures of serine and lysine are,



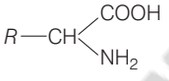
49 The increasing order of pK_a of the following amino acids in aqueous solution is Gly, Asp, Lys, Arg

(a) Asp < Gly < Arg < Lys (b) Arg < Lys < Gly < Asp
(c) Gly < Asp < Arg < Lys (d) Asp < Gly < Lys < Arg

[2019, 9 Jan Shift-II]

Ans.*(d)*

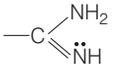
Amino acid molecules can be represented as,



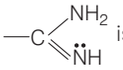
Nature of the '*R*' group will determine the basicity (hence, pK_a) of an amino acid.

	'R' in the amino group	Nature of *R*	Nature of the amino acids
1.	—$(CH_2)_3$—NH—C(NH_2^+)NH_2 (Arginine : Arg)	Basic	More basic (due to the presence of acetamidine group)
2.	—CH_2—C(=O)O^- (Aspartic acid: Asp)	Acidic	Acidic
3.	—H (Glycine) : Gly	Neutral	Neutral
4.	—$(CH_2)_4$—$\overset{+}{N}H_3$ (Lysine : Lys)	Basic	Basic

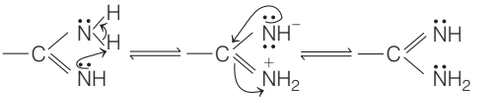
Acetamidine group present in arginine is



its self-protonation/deprotonation makes its conjugate acid very stable.

So,  is a strongly basic in nature.

The resonating structure of acetamidine group is



The basicity order of given amino acids in aqueous solution is as follows:

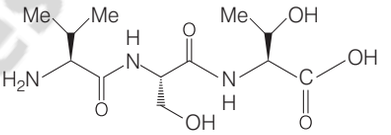
Asp < Gly < Lys < Arg

Thus, order of pK_a values is also,

Asp < Gly < Lys < Arg

pK_a value : (3) (6) (9.8) (10.8)

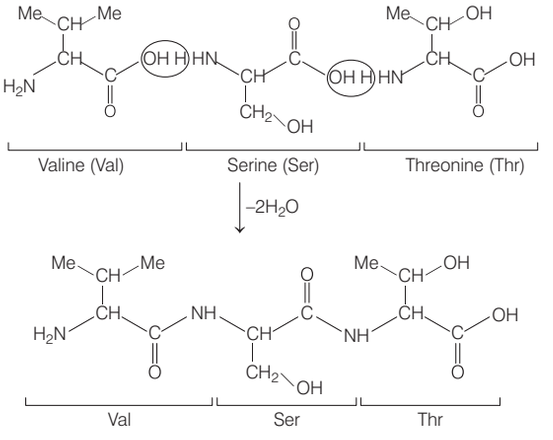
50 The correct sequence of amino acids present in the tripeptide given below is **[2019, 9 Jan Shift-II]**



(a) Thr - Ser - Leu (b) Leu - Ser - Thr
(c) Val - Ser - Thr (d) Thr - Ser - Val

Ans. ***(c)***

Formation of the tripeptide (Val-Ser-Thr) can be shown as:



51 Which of the following tests cannot be used for identifying amino acids ? **[2019, 10 Jan Shift-II]**

(a) Barfoed test (b) Ninhydrin test
(c) Xanthoproteic test (d) Biuret test

Ans. ***(a)***

(i) Barfoed test is used for detecting the presence of monosaccharides like glucose, fructose etc. Barfoed reagents is Cu (II) acetate solution.

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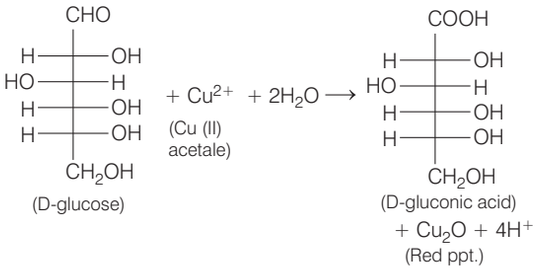
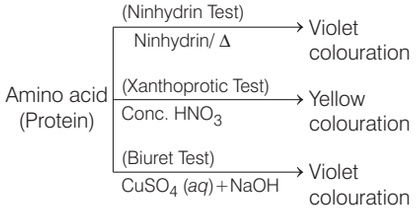


(ii)

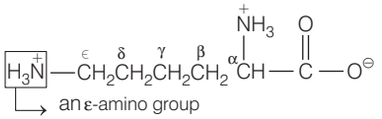


52 Among the following compounds, most basic amino acid is **[2019, 12 Jan Shift-I]**

(a) serine (b) asparagine (c) lysine (d) histidine

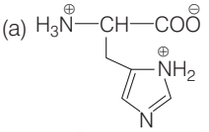
Ans. ***(c)***

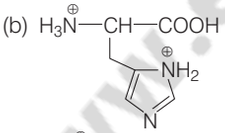
The most basic amino acid is lysine. There are only two basic amino acids (amino acids with two basic nitrogen containing groups). These are lysine and arginine. Lysine have an ε-amino group. At physiological pH, the groups are protonated as follows:

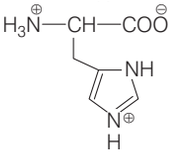


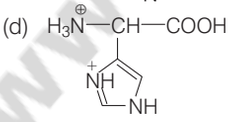
Asparagine is an acidic amino acid. It is the amide of aspartate.
Histidine is an imidazole substituted alanine.
Serine contain alcohol group and is an HO-substituted alanine.

53 The correct structure of histidine in a strongly acidic solution (pH = 2) is **[2019, 12 Jan Shift-II]**

(a) 

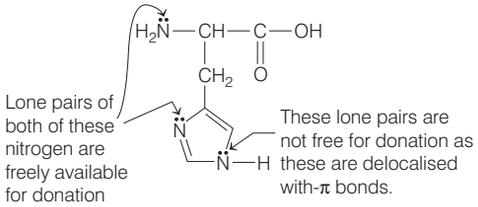
(b) 

(c) 

(d) 

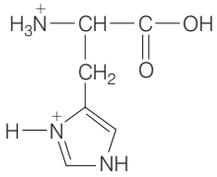
Ans. ***(d)***

Histidine has following structure in



At highly acidic pH, i.e. 2 both the nitrogens with lone pairs will accept one H^+ each and —C(=O)—OH will not loose its H^+.

Thus, the final structure of histidine at pH = 2 will be



54 The correct match between Item I and Item II is

	Item I		Item II
A.	Allosteric effect	P.	Molecule binding to the active site of enzyme.
B.	Competitive inhibitor	Q.	Molecule crucial for communication in the body.
C.	Receptor	R.	Molecule binding to a site other than the active site of enzyme.
D.	Poison	S.	Molecule binding to the enzyme covalently.

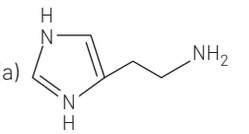
(a) A → P; B → R; C → S; D → Q
(b) A → P, B → R; C → Q; D → S
(c) A → R; B → P; C → S; D → Q
(d) A → R; B → P; C → Q; D → S **[2019, 11 Jan Shift-II]**

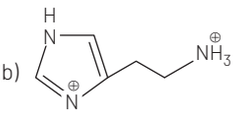
Ans. ***(d)***

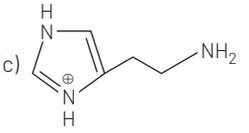
(A) Molecule binding to a site other than the active site of enzyme is called allosteric effect.
(B) Molecule binding to the active site of enzyme is called competitive inhibitor.
(C) Molecule crucial for communication in the body is called receptor.
(D) Molecule binding to the enzyme covalently is called poison.
Thus, the correct match is :

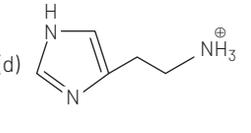
A → R, B → P, C → Q, D → S

55 The predominant form of histamine present in human blood is (pK_a, Histidine = 6.0) **[JEE Main 2018]**

(a) 

(b) 

(c) 

(d) 

Ans. ***(d)***

Our blood is slightly basic in nature with pH range from 7.35-7.4.
The structure of histamine is given below :

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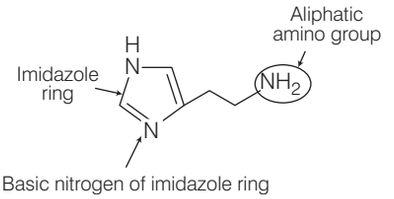
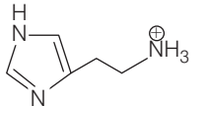


It is produced by decarboxylation of histidine having following structure.

It is clearly visible from the above structure that histamine has two basic centres namely aliphatic amino group and basic nitrogen of imidazole ring.

The aliphatic amino group has pK_a around 9.4.

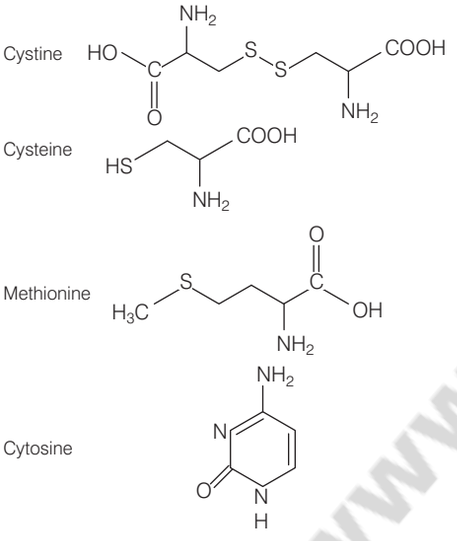
In blood with pH around 7.4 the aliphatic amino group of histamine become protonated to give a single charged cation as shown below



56 Thiol group is present in **[JEE Main 2016]**

(a) cystine (b) cysteine
(c) methionine (d) cytosine

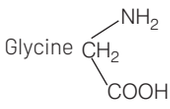
Ans. ***(b)***



57 Which one of the following statements is correct? **[AIEEE 2012]**

(a) All amino acids except lysine are optically active.
(b) All amino acids are optically active.
(c) All amino acids except glycine are optically active.
(d) All amino acids except glutamic acids are optically active.

Ans. ***(c)***



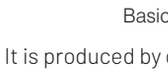
is α-amino acetic acid with no chiral carbon, thus optically inactive.

58 Biuret test is not given by **[AIEEE 2010]**

(a) carbohydrates (b) polypeptides
(c) urea (d) proteins

Ans. ***(a)***

Biuret test is characteristically given by the compound having



— NH — functional group.

59 The secondary structure of a protein refers to **[AIEEE 2007]**

(a) α-helical backbone
(b) hydrophobic interactions
(c) sequence of α-amino acids
(d) fixed configuration of the polypeptide backbone

Ans. ***(a)***

Primary structure involves sequence of α-amino acids in a polypeptide chain.

Secondary structure involves α-helical and β-pleated sheet like structures.

60 Identify the correct statement regarding enzymes. **[AIEEE 2004]**

(a) Enzymes are specific biological catalysts that can normally function at very high temperatures (T~ 1000 K)
(b) Enzymes are normally heterogeneous catalysts that are very specific in their action
(c) Enzymes are specific biological catalysts that cannot be poisoned
(d) Enzymes are specific biological catalysts that possess well defined active sites

Ans. ***(d)***

Normal optimum temperature of enzymes is between 25°C to 40°C. Hence (a) is false. Enzymes are normally homogeneous catalysts that can be poisoned.

Thus, (b) and (c) are also false. Enzymes have well defined active sites and their actions are specific in nature.

61 Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories ? **[AIEEE 2004]**

(a) A coenzyme (b) A hormone
(c) An enzyme (d) An antibiotic

Ans. ***(b)***

Insulin is a hormone built up of two polypeptide chains.

62 A substance forms Zwitter ion. It can have functional groups **[AIEEE 2002]**

(a) —NH_2, —COOH (b) —NH_2, —SO_3H
(c) Both (a) and (b) (d) None of these

Ans. ***(c)***

For the formation of Zwitter ion, basic part and acidic part both should be present in a molecule.

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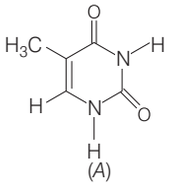
TOPIC 3
Vitamins and Nucleic Acids

63



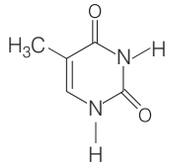
The compound 'A' is a complementary base of ..... in DNA stands. **[2021, 27 July Shift-I]**

(a) uracil (b) guanine
(c) adenine (d) cytosine

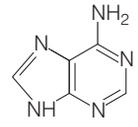
Ans. ***(c)***

Given structure of compound *A* is thymine, so its complementary base will be adenine.

Adenine form hydrogen bonds with thymine and cytosine will form hydrogen bond with guanine.

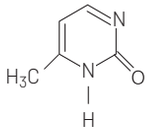


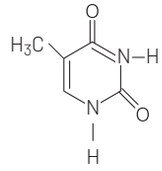
Thymine (Pyrimidine)

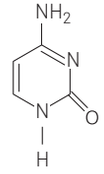


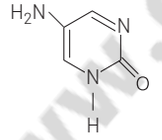
Adenine
(Purine base)

64 Which one of the following is correct structure for cytosine? **[2021, 25 July Shift-II]**

(a) 

(b) 

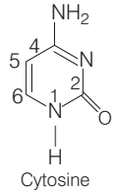
(c) 

(d) 

Ans. ***(c)***

Cytosine is one of four chemical bases in DNA and RNA.
It is a pyrimidine derivative, with a heterocylic aromatic ring and two substituents attached. The nucleoside of cytosine is cytidine.

Hence, correct structure of cytosine is,



Cytosine

65 Thiamine and pyridoxine are also known respectively as **[2021, 22 July Shift-II]**

(a) vitamin B_2 and vitamin E
(b) vitamin E and vitamin B_2
(c) vitamin B_6 and vitamin B_2
(d) vitamin B_1 and vitamin B_6

Ans. ***(d)***

Thiamine is also called vitamin B_1 and pyridoxine is also known as vitamin B_6.

Some common name of vitamins are as follows

Vitamin B_1 ⟶ Thiamine,
Vitamin B_6 ⟶ Pyridoxine
Vitamin B_2 ⟶ Riboflavin
Vitamin E ⟶ Tocopherol

66 Deficiency of vitamin K causes **[2021, 18 March Shift-II]**

(a) increase in blood clotting time
(b) increase in fragility of RBC's
(c) cheilosis
(d) decrease in blood clotting time

Ans. ***(a)***

Vitamin K deficiency causes increase in blood clotting time because their blood does not have enough vitamin K to form a clot. The bleeding can occur anywhere i.e. inside or outside the body.

Note : Vitamin K related to blood factor.

67 Which among the following pair of vitamins is stored in our body relatively for longer duration ? **[2021, 16 March Shift-I]**

(a) Thiamine and vitamin A (b) Vitamin A and vitamin D
(c) Thiamine and ascorbic acid (d) Ascorbic acid and vitamin D

Ans. ***(b)***

Vitamin A and vitamin D are stored in our body relatively for longer duration. These are water insoluble and soluble in fats and oils. Hence, these are called fat soluble vitamins.
Thiamine (vitamin B) and ascorbic acid (vitamin C) are water soluble vitamins and must be supplied regularly in diet. These vitamins are not stored in our body.

68 Which of the following vitamin is helpful in delaying the blood clotting ? **[2021, 26 Feb Shift-I]**

(a) Vitamin C (b) Vitamin B (c) Vitamin E (d) Vitamin K

Ans. ***(d)***

Deficiency of vitamin K increases blood clotting time. So, vitamin K is helpful in blood clotting. It is a fat-soluble vitamin.

Vitamin C is used to prevent and treat scurvy. It is a water soluble vitamin.

Vitamin B are also water soluble and play significant roles in cell metabolism and synthesis of RBC.

Vitamin E is a fat-soluble vitamin. Deficiency of it may cause increased fragility of RBCs, nerve problems and mascular weakness. Vitamin E is a fat-soluble anti-oxidant which protects cell membranes.

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69 Match List-I and List-II.

	List-I		List-II
A.	Valium	1.	Antifertility drug
B.	Morphine	2.	Pernicious anaemia
C.	Norethindrone	3.	Analgesic
D.	Vitamin B_{12}	4.	Tranquiliser

Choose the correct answer from the option given below. **[2021, 24 Feb Shift-II]**

	A	B	C	D
(a)	4	3	2	1
(b)	4	3	1	2
(c)	2	4	3	1
(d)	1	3	4	2

Ans. ***(b)***

(A) Valium – (4) Tranquilizer

A tranquilizer drug became a standard drug for the treatment of anxiety and one of most commonly prescribed drugs of all time.

(B) Morphine – (3) Analgesic

Morphine is effective for both acute and chronic pain and often used before and after surgery.

(C) Norethindrone – (1) Antifertility drug

It is a form of progesterone, a female hormone important for regulating ovulation and menstruation.

(D) Vitamin B_{12} –(2) Pernicious anaemia

It is a nutrient that helps to keep our body blood cells and nerve cells healthy and help in making DNA.

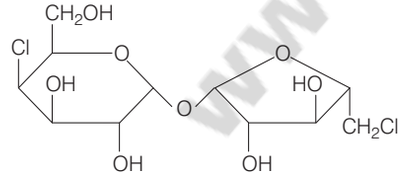
70 Which of the following will react with $CHCl_3$ + alc. KOH? **[2020, 4 Sep Shift-I]**

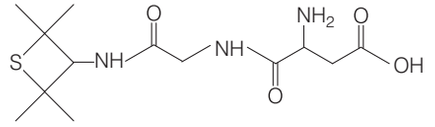
(a) Adenine and lysine (b) Thymine and proline

(c) Adenine and thymine (d) Adenine and proline

Ans. ***(a)***

Adenine and lysine react with $CHCl_3$ and alc. KOH. This type of reagent show carbylamine reaction. Carbylamine reaction is given by only primary amine.



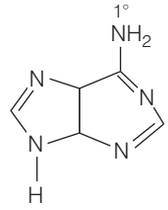


General reaction is as follows :

$$\underset{1^\circ \text{ amine}}{R\text{—}NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{Isocyanide}{R\text{—}N \equiv C} + 3KCl + 3H_2O$$

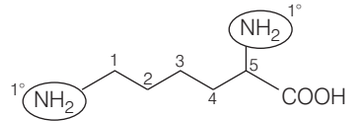
Adenine and lysine both have primary amine.

(a) **Adenine**



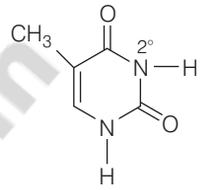
In this structure, primary amine is present. Thus, it shows carbylamine reaction.

Lysine



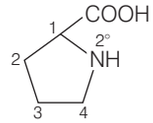
Here, 2 primary amine are present, thus it show carbylamine reaction.

(b) **Thymine**



Here, secondary amine (2°) are present, thus it doesn't show carbylamine reaction.

Proline Cyclic amino acid



Here, secondary amine (2°) are present, thus it doesn't show carbylamine reaction.

(c) Adenine show this reaction but thymine does not show this reaction with carbylamine reaction.

(d) Adenine It show the reaction with carbylamine reaction but proline does not show reaction.

71 Match the following :

(i)	Riboflavin	(A)	Beriberi
(ii)	Thiamine	(B)	Scurvy
(iii)	Pyridoxine	(C)	Cheilosis
(iv)	Ascorbic acid	(D)	Convulsions

[2020, 7 Jan Shift-I]

(a) (i)-(C), (ii)-(D), (iii)-(A), (iv)-(B)

(b) (i)-(C), (ii)-(A), (iii)-(D), (iv)-(B)

(c) (i)-(D), (ii)-(B), (iii)-(A), (iv)-(C)

(d) (i)-(A), (ii)-(D), (iii)-(C), (iv)-(B)

Ans. ***(b)***

(i) Riboflavin - (C) Cheilosis

(ii) Thiammine - (A) Beri-beri

(iii) Pyridoxine - (D) Convulsions

(iv) Ascorbic acid - (B) Scurvy

Thus, the correct option is (b).

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72 Which of the following statement is not true about RNA? **[2019, 12 April Shift-I]**

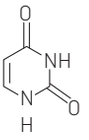
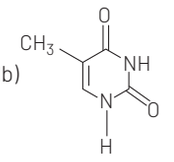
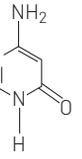
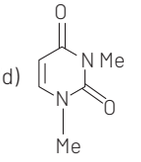
(a) It controls the synthesis of protein
(b) It has always double stranded α-helix structure
(c) It usually does not replicate
(d) It is present in the nucleus of the cell

Ans. ***(b)***

RNA does not have double stranded α-helix structure. Helixes present in RNA are single-stranded but sometimes they fold back on themselves to form a double helix structure. RNA usually does not replicate.

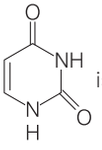
It is present in the nucleus of the cell. It controls the synthesis of protein. RNA molecules are of three types, i.e. messenger's RNA (*m*-RNA), ribosomal RNA (*r*RNA), transfer RNA (*t*-RNA).

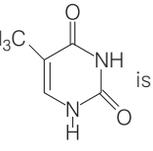
73 Among the following compounds, which one is found in RNA? **[2019, 11 Jan Shift-I]**

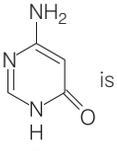
(a) 
(b) 
(c) 
(d) 

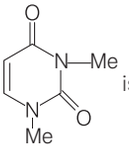
Ans. ***(a)***

RNA contains, adenine (A), guanine (G), cytosine (C) and uracil (U).
In the given options,

(a)  is uracil (present in RNA only)

(b)  is thymine (present in DNA only)

(c)  is cytosine (present in both DNA and RNA)

(d)  is not a pyrimidine base but a derivative of uracil.

74 Which of the vitamins given below is water soluble? **[JEE Main 2015]**

(a) Vitamin C (b) Vitamin D
(c) Vitamin E (d) Vitamin K

Ans. ***(a)***

Vitamin B and C are water soluble while vitamin A,D,E and K are fat soluble or water insoluble.

75 Which one of the following bases is not present in DNA? **[JEE Main 2014]**

(a) Quinoline
(b) Adenine
(c) Cytosine
(d) Thymine

Ans. ***(a)***

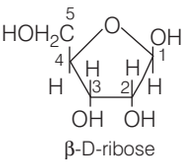
DNA contains four nitrogenous pyramidine bases, adenine, guanine, cytosine, thymine. While quinoline is an alkaloid, hence, it is not present in DNA.

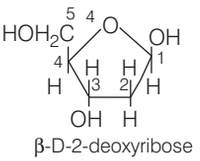
76 The presence or absence of hydroxy group on which carbon atom of sugar differentiates RNA and DNA? **[AIEEE 2011]**

(a) 1st (b) 2nd
(c) 3rd (d) 4th

Ans. ***(b)***

In RNA molecule, sugar moiety is β-D-ribose in which —OH group is present at 2nd carbon. Whereas in DNA, it is β-D-2-deoxyribose in which— OH group is absent at 2nd carbon.


β-D-ribose

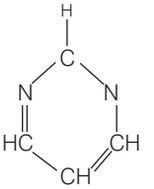

β-D-2-deoxyribose

77 The pyrimidine bases present in DNA are **[AIEEE 2006]**

(a) cytosine and adenine
(b) cytosine and guanine
(c) cytosine and thymine
(d) cytosine and uracil

Ans. ***(c)***

In DNA, cytosine and thymine are pyrimidine bases.


Pyrimidine base

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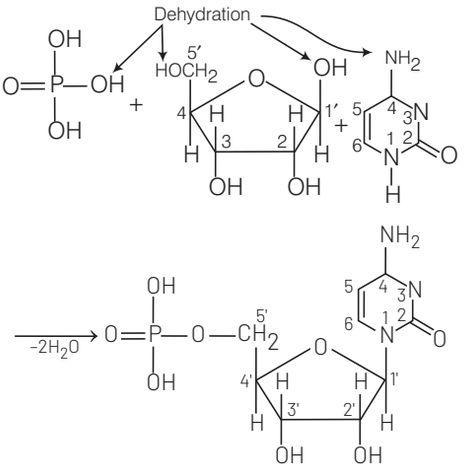
78 In both DNA and RNA, heterocylic base and phosphate ester linkages are at **[AIEEE 2005]**

(a) C'_5 and C'_1 respectively of the sugar molecule
(b) C'_1 and C'_5 respectively of the sugar molecule
(c) C'_2 and C'_5 respectively of the sugar molecule
(d) C'_5 and C'_2 respectively of the sugar molecule

Ans. ***(a)***

Synthesis of RNA/DNA from phosphoric acid, ribose and cytosine is given below. Thus, ester linkages are at C'_5 and C'_1 of sugar molecule.



79 Which base is present in RNA but not in DNA? **[AIEEE 2004]**

(a) Uracil (b) Cytosine (c) Guanine (d) Thymine

Ans. ***(a)*** Uracil is present in RNA but not in DNA.

80 The reason for double helical structure of DNA is operation of **[AIEEE 2003]**

(a) van der Waals' forces (b) dipole-dipole interaction
(c) hydrogen bonding (d) electrostatic attractions

Ans. ***(c)***

Hydrogen bonding is involved as a molecular force in the DNA molecule.

Watson and Crick observed the purine- pyrimidine type of hydrogen bonding (instead of purine-purine and pyrimidine-pyrimidine type).

81 RNA contains **[AIEEE 2002]**

(a) ribose sugar and thymine
(b) ribose sugar and uracil
(c) deoxyribose sugar and uracil
(d) deoxyribose sugar and thymine

Ans. ***(b)***

RNA, Ribonucleic acid.

Sugar present in RNA is D (–) ribose. It consists of cytosine and uracil as pyrimidine and guanine and adenine as purine bases.

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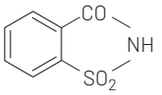
29

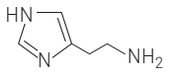
Chemistry in Everyday Life

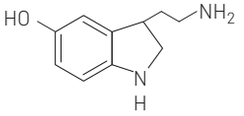
TOPIC 1
Chemicals in Medicines

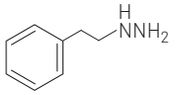
01 Which one of the following chemicals is responsible for the production of HCl in the stomach leading to irritation and pain?

[2021, 27 Aug Shift-II]

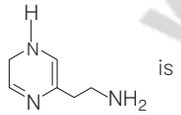
(a) 

(b) 

(c) 

(d) 

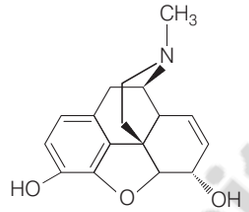
Ans. ***(b)***

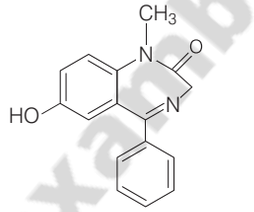
The compound  is responsible for the production

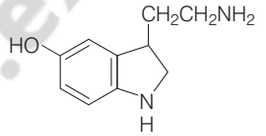
of HCl in the stomach leading to irritation and pain.

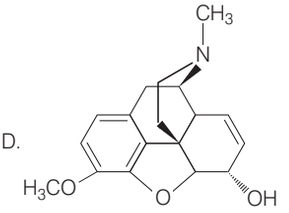
So, the option (b) is correct.

02 Consider the following structures :

A. 

B. 

C. 

D. 

The correct statement about (A), (B), (C) and (D) is

[2021, 27 Aug Shift-I]

(a) (A), (B) and (C) are narcotic analgesics

(b) (B), (C) and (D) are tranquillizers

(c) (A) and (D) are tranquillizers

(d) (B) and (C) are tranquillizers

Ans. ***(d)***

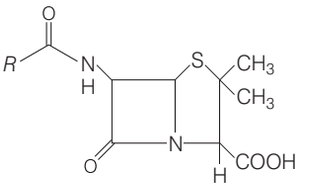
The structures A and D are narcotic analgesics, where A is morphine and D is codeine.

The structures B and C are tranquillizers *viz*. diazepam and serotonin respectively.

03 Given below are two statements.

Statement I Penicillin is a bacteriostatic type antibiotic.

Statement II The general structure of penicillin is



Choose the correct option.

[2021, 27 July Shift-II]

(a) Both statement I and statement II are false

(b) Statement I is false but statement II is true

(c) Both statement I and statement II are true

(d) Statement I is true but statement II is false

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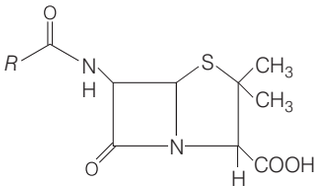
Ans. ***(b)***

Penicillin kills the bacteria, therefore it is a bactericidal type antibiotic.

The structure of penicillin is



∴ Statement I is false and statement II is true.

04 Match List-I with List-II.

	List-I (Drug)		List-II (Class of drug)
A.	Furacin	I.	Antibiotic
B.	Arsphenamine	II.	Tranquilisers
C.	Dimetone	III.	Antiseptic
D.	Valium	IV.	Synthetic antihistamines

Choose the most appropriate match : **[2021, 27 July Shift-I]**

	A	B	C	D		A	B	C	D
(a)	I	III	IV	II	(b)	III	IV	II	I
(c)	II	I	III	IV	(d)	III	I	IV	II

Ans. ***(d)***

A. Furacin acts as antiseptic which is applied to wounds, cuts, ulcers etc. to prevent the growth of micro-organisms.

B. Arsphenamine also known as salvarsan acts as antibiotic, a drug effective against syphilis was introduced at beginning of 1910 but have now been supplanted by modern antibiotics.

C. Dimetone is synthetic antihistamines. They interfere with natural action of histamines by competing with histamine for binding sites of receptor where histamine exerts its effect.

D. Valium is tranquilisers (neurologically active drug).

Hence, correct match is A → III, B → I, C → IV, D → II.

05 Match List-I with List-II.

	List-I		List-II
A.	Be	1.	Treatment of cancer
B.	Mg	2.	Extraction of metals
C.	Ca	3.	Incendiary bombs and signals
D.	Ra	4.	Windows of X-ray tubes
		5.	Bearings for motor engines.

Choose the most appropriate answer the option given below. **[2021, 18 March Shift-II]**

	A	B	C	D		A	B	C	D
(a)	4	3	1	2	(b)	4	3	2	1
(c)	3	4	5	2	(d)	3	4	2	5

Ans. ***(b)***

(A) Metallic beryllium is used for making windows of *X*-ray tubes.

(B) When Mg combined with water while burning it releases gas and oxygen. Magnesium is used in either powdered or solid form as an incendiary agent for both illumination and antipersonnel purposes.

(C) Pure calcium metal is used as a reducing agent in the extraction of other types of metal, such as thorium, uranium and zirconium.

(D) Due to its radioactive nature Ra is used in the treatment of cancer.

Hence, correct match is (A-4), (B-3), (C-2), (D-1).

06 Match List-I with List-II.

	List-I (Class of chemicals)		List-II (Example)
A.	Antifertility drug	1.	Meprobamate
B.	Antibiotic	2.	Alitame
C.	Tranquilizer	3.	Norethindrone
D.	Artificial sweetener	4.	Salvarsan

[2021, 18 March Shift-II]

	A	B	C	D		A	B	C	D
(a)	2	3	4	1	(b)	4	3	2	1
(c)	3	4	1	2	(d)	2	4	1	3

Ans. ***(c)***

(A) Antifertility drug → Norethindrone

Norethindrone is a synthetic progesterone which is amongst the most commonly used antifertility drugs.

(B) Antibiotic → Salvarsan

Arsphenamine, also known as salvarsan used as antibiotic.

(C) Tranquilizer → Meprobamate

Meprobamate is used to treat anxiety disorders or for short-term relief of the symptoms of anxiety in adults and children 6 years of age and older. Meprobamate is in a class of medications called tranquilizers.

(D) Artificial sweetener → Alitame

Alitame is an artificial sweetener containing aspartic acid.

Hence, correct match is (A-3), (B-4), (C-1), (D-2).

07 Match the list-I with list- II

	List-I		List-II
(A)	Chlorophyll	(i)	Ruthenium
(B)	Vitamin-B_{12}	(ii)	Platinum
(C)	Anticancer drug	(iii)	Cobalt
(D)	Grubbs catalyst	(iv)	Magnesium

Choose the most appropriate answer from the options given below **[2021, 18 March Shift-I]**

	A	B	C	D
(a)	(iii)	(ii)	(iv)	(i)
(b)	(iv)	(iii)	(ii)	(i)
(c)	(iv)	(iii)	(i)	(ii)
(d)	(iv)	(ii)	(iii)	(i)

Ans. ***(b)***

A. Chlorophyll is coordination complex of Mg.

B. Vitamin B_{12}, cyanocobalamine is a coordination compound of cobalt.

C. *cis*-platin $[Pt(NH_3)_2Cl_2]$ used in the treatment of cancer and is a coordination compound of platinum.

D. Grubbs catalyst is a series of catalysts containing ruthenium.

∴ Correct match is (A-iv), (B-iii), (C-ii), (D-i)

08 Match the List-I with List- II.

	List-I (Class of drug)		List-II (Example)
(A)	Antacid	(i)	Novestrol
(B)	Artificial sweetener	(ii)	Cimetidine
(C)	Antifertility	(iii)	Valium
(D)	Tranquilizers	(iv)	Alitame

[2021, 18 March Shift-I]

	A	B	C	D
(a)	(ii)	(iv)	(i)	(iii)
(b)	(iv)	(i)	(ii)	(iii)
(c)	(iv)	(iii)	(i)	(ii)
(d)	(ii)	(iv)	(iii)	(i)

Ans. ***(a)***

A. Antacid – Cimetidine

Cimetidine is a stomach acid reducer that is used to treat and prevent certain types of stomach ulcer.

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B. Artificial sweetener – Alitame
Alitame is an aspartic acid containing dipeptide sweetener.

C. Antifertility – Novestrol
Antifertility drugs is a chemical substances which suppress the action of hormones that promote pregnancy.
An antifertility drug is novestrol (ethynylestradiol). Another example of antifertility drugs is norethindrone.

D. Tranquilizers – Valium
Valium, trade name of a tranquiliser drug introduced by the pharmaceutical company Hofmann-La-Roche in 1963.

∴ Correct match is A-(ii), B-(iv), C-(i), D-(iii)

09 With respect to drug-enzyme interaction, identify the wrong statement **[2021, 17 March Shift-I]**

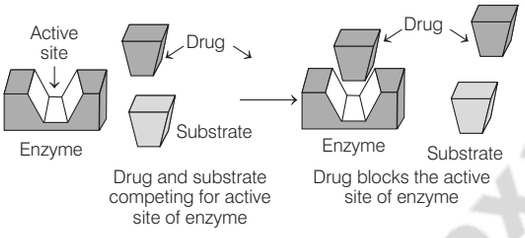
(a) Non-competitive inhibitor binds to the allosteric site.
(b) Allosteric inhibitor changes the enzyme's active site.
(c) Allosteric inhibitor competes with the enzyme's active site.
(d) Competitive inhibitor binds to the enzyme's active site.

Ans. ***(c)***

Allosteric inhibitor combines at allosteric site and not the active site.

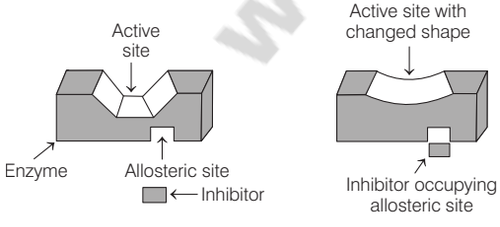
Drugs inhibit the attachment of substrate on active site of enzymes in two different ways;

(i) Drugs compete with the natural substrate for their attachment on the active sites of enzymes. Such drugs are called competitive inhibitors.



Drug and substrate competing for active site

(ii) Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site. This binding of inhibitor at allosteric site changes the shape of the active site in such a way that substrate cannot recognise it. This is also called non-competitive inhibitor.

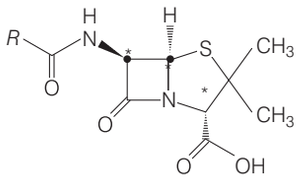


Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site.

10 The number of chiral centres in penicillin is ..... . **[2020, 8 Jan Shift-I]**

Ans. ***(3.00)***

Penicillin



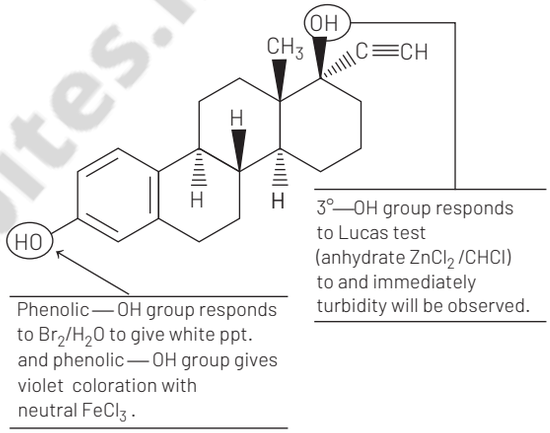
There are three chiral centres shown by asterisk sign.

11 The antifertility drug "Novestrol" can react with **[2020, 3 Sep Shift-I]**

(a) $ZnCl_2$ / HCl; $FeCl_3$; alcoholic HCN
(b) Br_2 /water; $ZnCl_2$ / HCl; $FeCl_3$
(c) alcoholic HCN; NaOCl; $ZnCl_2$ / HCl
(d) Br_2 /water; $ZnCl_2$ / HCl; NaOCl

Ans. ***(b)***

The antifertility drug "novestrol" or ethinylestradiol has the following structure :



So, the correct combination of reagents is in option (b).

i.e. Br_2/water, $ZnCl_2$/HCl and $FeCl_3$.

12 Match the following drugs with their therapeutic actions :

(i)	Ranitidine	(a)	Antidepressant
(ii)	Nardil (Phenelzine)	(b)	Antibiotic
(iii)	Chloramphenicol	(c)	Antihistamine
(iv)	Dimetane (Brompheniramine)	(d)	Antacid
		(e)	Analgesic

[2020, 3 Sep Shift-II]

(a) (i)-(a); (ii)-(c); (iii)-(b); (iv)-(e)
(b) (i)-(e); (ii)-(a); (iii)-(c); (iv)-(d)
(c) (i)-(d); (ii)-(a); (iii)-(b); (iv)-(c)
(d) (i)-(d); (ii)-(c); (iii)-(a); (iv)-(e)

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Ans. ***(c)***

Correct match is

(i)→(d), (ii)→(a), (iii)→(b) and (iv)→(c)

(i) Ranitidine → Antacid
[Ranitidine, in which backward flow of acid occur from stomach.]

(ii) Nardil (Phenelzine) → Antidepressant.
[It is used as an antidepressant and anxiotytic]

(iii) Chloramphenicol → Antibiotic
[It is an antibiotic used for treatment of bacterial infections]

(iv) Dimetane (Brompheniramine) → Antihistamine
[It is used for treatment of the symptoms of common cold and allergic such as runny nose, itchy eyes etc.]

13 The mechanism of action of "Terfenadine" (Seldane) is

(a) Inhibits the secretion of histamine **[2020, 4 Sep Shift-II]**
(b) Inhibits the action of histamine receptor
(c) Helps in the secretion of histamine
(d) Activates the histamine receptor

Ans. ***(b)***

Seldane (Terfenadine) is also an antihistamines drug. which interfere with the natural action of histamine by competing with histamine for binding sites of receptors, where histamine acts. Thus, it do not affect the secretion of acid in stomach but compete with histamine where histamine exterts its effect.

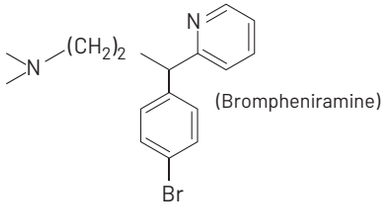
14 If a person is suffering from the deficiency of nor-adrenaline, what kind of drug can be suggested? **[2020, 5 Sep Shift-I]**

(a) Antihistamine (b) Analgesic
(c) Antidepressant (d) Anti-inflammatory

Ans. ***(c)***

Nor-adrenaline is one of the neurotransmitter that plays an important role in mood changes. If the level of nor-adrenaline in the body is low for some reason, then the signal-sending activity becomes low and the person suffers from depression. In such cases, antidepressant drugs are needed. These drugs inhibit the enzymes which catalyse the degradation of nor-adrenaline. If the enzyme is inhibited, this important neurotransmitter is slowly metabolised and can activate its receptor for longer period of time, thus counteracting the effect of depression. Iproniazid and phenelzine are two such antidepressant drugs.

15 The following molecule acts as an



(Brompheniramine)

[2020, 5 Sep Shift-II]

(a) antiseptic (b) anti-depressant
(c) anti-bacterial (d) anti-histamine

Ans. ***(d)***

Synthetic Brompheniramine is an antihistamine that is used to treat sneezing, runny nose and itchy or watery eyes caused by allergies, hay fever and the common cold.

16 The presence of soluble fluoride ion upto 1 ppm concentration in drinking water, is **[2020, 6 Sep Shift-I]**

(a) harmful for teeth
(b) harmful to skin
(c) harmful to bones
(d) safe for teeth

Ans. ***(d)***

According to WHO, optimal fluoride ion concentration is 0.5 to 1 ppm in drinking water is safe and good for enamel of teeth and it makes teeth much harder.

Hence, the correct option is (d).

17 Noradrenaline is a/an **[2019, 9 April Shift-II]**

(a) antidepressant
(b) antihistamine
(c) neurotransmitter
(d) antacid

Ans. ***(c)***

Noradrenaline is one of the example of neurotransmitters. It plays a major role in mood changes. If the level of noradrenaline is low for some reason, then signal-sending activity becomes low and the person suffers from depression.

18 The correct match between item (I) and item (II) is

	Item - I		Item - II
(A)	Norethindrone	(P)	Antibiotic
(B)	Ofloxacin	(Q)	Antifertility
(C)	Equanil	(R)	Hypertension
		(S)	Analgesics

[2019, 11 Jan Shift-I]

(a) (A)→(Q); (B)→(R); (C)→(S)
(b) (A)→(Q); (B)→(P); (C)→(R)
(c) (A)→(R); (B)→(P); (C)→(S)
(d) (A)→(R); (B)→(P); (C)→(R)

Ans. ***(b)***

The correct match is :

A→(Q), B→(P), C→(R)

(A) Norethindrone It is an antifertility drug(*Q*) containing synthetic progesterone derivative. [Other similar drug, is ethinylestradiol (novestrol)].

(B) Ofloxacin It is an antibiotic (*P*), i.e produced wholly or partly by chemical synthesis with low concentration of microorganism. [Some other similar drugs : Penicillin, chloramphenicol, salvarsan etc.]

(C) Equanil (meprobamate) It is a mild tranquilizer for relieving hypertension. It relieve anxiety, stress, excitement by inducing a sense of well being.
(Other similar drug is chlordiazepoxide.)

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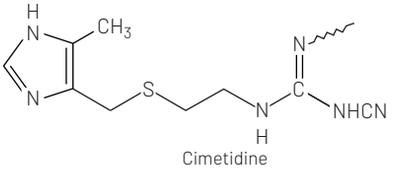
19 Which of the following compounds is not an antacid? **[JEE Main 2015]**

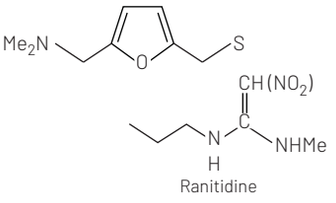
(a) Aluminium hydroxide
(b) Cimetidine
(c) Phenelzine
(d) Ranitidine

Ans. ***(c)***

Aluminium hydroxide $Al(OH)_3$, cimetidine and ranitidine are antacids while phenelzine is not.

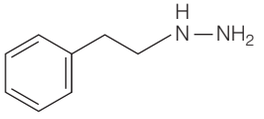


Cimetidine



Ranitidine

Phenelzine is a tranquilizer, not an antacid.



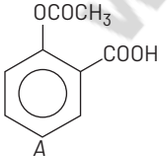
20 Which one of the following types of drugs reduces fever ? **[AIEEE 2005]**

(a) Tranquiliser (b) Antibiotic
(c) Antipyretic (d) Analgesic

Ans. ***(c)***

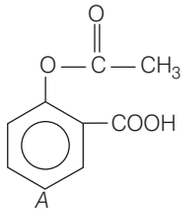
Antipyretic drugs reduce fever. Analgesic relieve in pain, antibiotics act against bacterial infections while tranquilisers are used against mental disorders.

21 Compound *A* given below is **[AIEEE 2002]**



(a) antiseptic (b) antibiotic
(c) analgesic (d) pesticide

Ans. ***(c)***



o-acetyl salicylic acid
aspirin (Analgesic)

TOPIC 2
Chemicals in Food

22 Match List-I and List-II.

	List-I (Chemical compound)		List-II (Used as)
A.	Sucralose	1.	Synthetic detergent
B.	Glyceryl ester of stearic acid	2.	Artificial sweetener
C.	Sodium benzoate	3.	Antiseptic
D.	Bithionol	4.	Food preservative

Choose the correct match. **[2021, 17 March Shift-II]**

	A	B	C	D		A	B	C	D
(a)	4	3	2	1	(b)	2	1	4	3
(c)	3	2	4	1	(d)	1	2	4	3

Ans. ***(b)***

The correct matches are A-2, B-1, C-4, D-3.

A. Sucralose → Artificial sweetener
Artificial sweetener is the sugar that is sweet like sugar but has zero or low calories. Artificial sweeteners can be plant extract or chemical synthesised. Saccharin, aspartame, sodium cyclamate and sucralose are the examples of artificial sweeteners.

B. Glyceryl ester of stearic acid → Synthetic detergent Esters of stearic acid are used in synthesis of soaps and detergents.

C. Sodium benzoate → Food preservative
The food is oxidised or hydrolysed by several factors such as air that is known as aerial oxidation, or by moisture, bacteria and light.
Sodium benzoate has an aromatic ring that can stabilise the free radical which causes the oxidation of food. Sodium benzoate is a food preservative.

D. Bithionol → Antiseptic
Bithionol is added to soap to impart antiseptic property. It reduces odour produced by bacterial decomposition of organic matter on the skin.

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23 A chemist has 4 samples of artificial sweetener *A*, *B*, *C* and *D*. To identify these samples, he performed certain experiments and noted the following observations :

(i) *A* and *D* both form blue-violet colour with ninhydrin.

(ii) Lassaigne extract of *C* gives positive $AgNO_3$ test and negative $Fe_4[Fe(CN)_6]_3$ test.

(iii) Lassaigne extract of *B* and *D* gives positive sodium nitroprusside test.

Based on these observations which option is correct?

[2020, 8 Jan Shift-I]

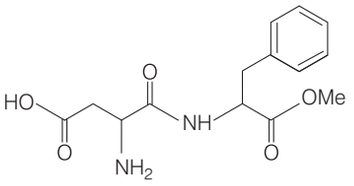
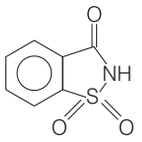
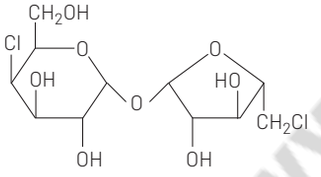
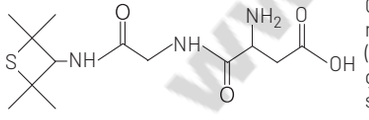
(a) *A* : Alitame; *B* : Saccharin ; *C* : Aspartame; *D* : Sucralose

(b) *A* : Saccharin; *B* : Alitame; *C* : Sucralose; *D* : Aspartame

(c) *A* : Aspartame; *B* : Alitame;

Ans. ***(d)***

Based on the observations, given in question, *A* : Aspartame, *B* : Saccharin, *C* : Sucralose, *D* : Alitame.

(*A*)	Aspartame		Gives ninhydrin test (has amino group).
(*B*)	Saccharin		Positive test for S (sodium nitroprusside test)
(*C*)	Sucralose		Positive $AgNO_3$ test due to Cl and no nitrogen ∴ negative $Fe_4[Fe(CN)_6]_3$ test.
(*D*)	Alitame		Gives ninhydrin test (has amino group) and sodium nitroprusside test (has sulphur).

TOPIC 3
Cleaning Agents

24 Which one of the following chemical agent is not being used for dry cleaning of clothes ?

[2021, 25 July Shift-I]

(a) H_2O_2 (b) CCl_4 (c) Liquid CO_2 (d) $Cl_2C=CCl_2$

Ans. ***(b)***

CCl_4 (carbon tetrachloride) was commonly blended with other solvents for use as a dry cleaning solvent. Due to its high toxicity and tendency to corrode equipment. Carbon tetrachloride is no longer used as a dry cleaning solvent.

Other solvents are,

H_2O_2 - Bleaching agent in laundry.

CO_2 - Dry cleaning agent for clothes.

$CCl_2=CCl_2$ → Dry cleaning agent for clothes.

25 Sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$ is an anionic surfactant which forms micelles in oil.

Choose the correct statement for it from the following.

[2021, 22 July Shift-I]

(a) It forms spherical micelles with $CH_3(CH_2)^-_{16}$ group pointing towards the centre of sphere.

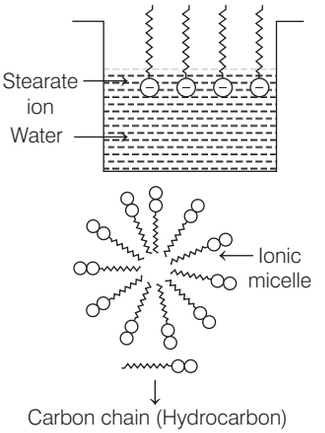
(b) It forms non-spherical micelles with —COO^- group pointing outwards on the surface.

(c) It forms spherical micelles with $CH_3(CH_2)^-_{16}$ group pointing outwards on the surface of sphere

(d) It forms non-spherical micelles with $CH_3(CH_2)^-_{16}$ group pointing towards the centre.

Ans. ***(a)***

Micelles formed are spherical with hydrocarbon part towards the centre of sphere.



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The formation of a micelle is a response to the amphipathic nature of fatty acids, meaning that they contain both hydrophilic regions (polar head groups) as well as hydrophobic regions (the long hydrophobic chain).

26 Green chemistry in day-to-day life is in the use of

[2021, 20 July Shift-I]

(a) chlorine for bleaching of paper.
(b) large amount of water alone for washing clothes.
(c) Tetrachloroethene for laundry.
(d) Liquified CO_2 for dry cleaning of clothes.

Ans. ***(d)***

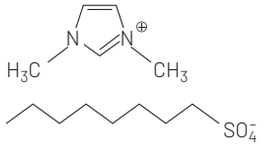
Liquified CO_2 for dry cleaning of clothes is in the use of green chemistry in day to day life.

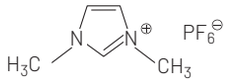
Chlorine gas was used earlier for bleaching paper. Now a days, hydrogen peroxide (H_2O_2) with suitable catalyst are used.

Earlier solvents like tetrachloroethylene were used in dry cleaning of clothes but they pollute the ground water and are carcinogenic.

27 An ionic micelle is formed on the addition of

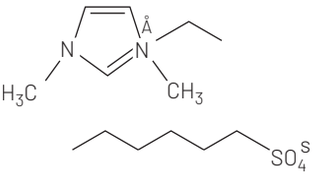
[2020, 3 Sep Shift-II]

(a) 

(b) liquid diethyl ether to aqueous NaCl solution
(c) sodium stearate to pure toluene excess water to liquid
(c) 

Ans. ***(a)***

An ionic micelle is formed due to presence of hydrophobic chain. It can easily be formed by the addition of



28 Which of the following is an anionic detergent?

[JEE Main 2016]

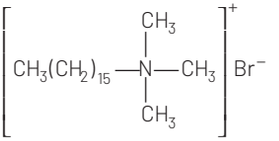
(a) Sodium lauryl sulphate
(b) Cetyltrimethyl ammonium bromide
(c) Glyceryl oleate
(d) Sodium stearate

Ans. ***(a)***

Sodium lauryl sulphate $[(CH_3(CH_2)_{10}CH_2OSO_3^-Na^+)]$

= Anionic detergent

Cetyltrimethyl ammonium bromide



= Cationic detergent

Glyceryl oleate $[(C_{17}H_{32}COO)_3C_3H_5]$

= Non-ionic detergent

Sodium stearate $[C_{17}H_{35}COO^-Na^+]$

= Anionic soap

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30

Principles Related to Practical Chemistry

TOPIC 1
Detection of Extra Elements and Functional Groups

01 Which one of the following tests used for the identification of functional groups in organic compounds does not use copper reagent ?

[2021, 27 Aug Shift-II]

(a) Barfoed's test
(b) Seliwanoff's test
(c) Benedict's test
(d) Biuret test for peptide bond

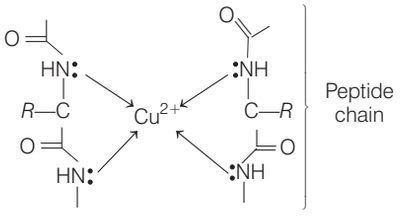
Ans. ***(b)***

Barfoed's test is used to detect monosaccharides.
In this test, the aldehyde group of monosaccharides reduces Cu(II) acetate to Cu(I) oxide which result in the formation of brick red ppt.

$$RCHO + 2\,Cu^{2+} + H_2O \longrightarrow RCOOH + \underset{\text{(ppt.)}}{Cu_2O\downarrow} + 4H^+$$

Benedict's test is used to test the presence of reducing sugar. Copper (II) sulphate is used in Barfoed's test.

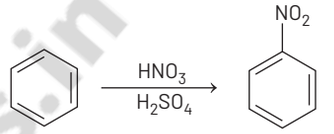
Biuret test is used to test the presence of peptide bond. The biuret reagent contains hydrated copper sulphate, sodium hydroxide and Rochelle salt (sodium-potassium tartarate). When the aqueous, solution of protein is treated with this reagent, the solution turns purple confirming the presence of amide bond.



Chelated complex of Cu^{2+} ions formed gives purple colour to the solution.

So, correct answer is option (b) Seliwanoff's test which is used to distinguish between ketoses and aldoses. The Seliwanoff's reagent contains resorcinol and HCl.

02



In the above reaction 3.9 g of benzene on nitration gives 4.92 g of nitrobenzene. The percentage yield of nitrobenzene in the above reaction is ..... % (Round off to the nearest integer).

(Given, atomic mass C : 12.0 u, H : 1.0 u, O : 16.0 u, N : 14.0 u)

[2021, 17 March Shift-I]

Ans. ***(80)***

$$C_6H_6 \xrightarrow[H_2SO_4]{HNO_3} C_6H_5NO_2 \qquad \text{(Molar mass = 123)}$$

Moles of $C_6H_6 = \left(\frac{3.9}{78}\right) = 0.05$

So, moles of $C_6H_5NO_2$ formed should be $\frac{3.9}{78}$.

Mass of $C_6H_5NO_2$ = Moles × Molar mass

$$= \frac{3.9}{78} \times 123 = 6.15\,g$$

By conserving moles of carbon, mole or $C_6H_5NO_2$.

$$\% \text{ yield} = \frac{\text{Weight actually formed}}{\text{Weight theoretical}} \times 100$$

$$= \frac{4.92}{6.15} \times 100 = 80\%$$

03 In Duma's method of estimation of nitrogen, 0.1840 g of an organic compound gave 30 mL of nitrogen collected at 287 K and 758 mm of Hg pressure. The percentage composition of nitrogen in the compound is ..... . (Round off to the nearest integer).

[Given: Aqueous tension at 287 K = 14 mm of Hg]

[2021, 16 March Shift-II]

Ans. ***(19)***

Given, mass of organic compound 0.1840 g
Total pressure = 758 mm of Hg
Aqueous tension = 14 mm of Hg

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Partial pressure of dry N_2 = 758 – 14 = 744 mm of Hg

For N_2,

$V = 30\ mL = 0.03\ L$

$T = 287\ K$

$p = 744\ mm\ of\ Hg = \frac{744}{760}\ atm$

So, moles of N_2 $(n) = \frac{pV}{RT} = \frac{744}{760} \times \frac{0.03}{0.0821 \times 287}$

$n = 1.25 \times 10^{-3}$ moles of N_2

Weight of N_2 = Moles × Molar mass

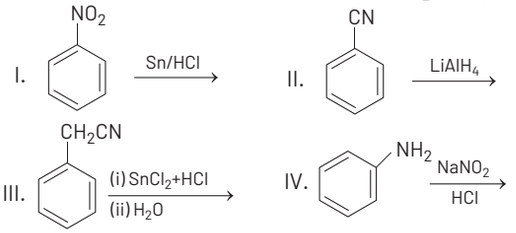
$= 1.25 \times 10^{-3} \times 28 = 35 \times 10^{-3}$ g

% composition of N_2

$= \frac{\text{Mass of } N_2}{\text{Mass of organic compound}} \times 100 = \frac{35 \times 10^{-3}}{0.1840} \times 100 = 19\%$

04 The Kjeldahl method of nitrogen estimation fails for which of the following reaction products?

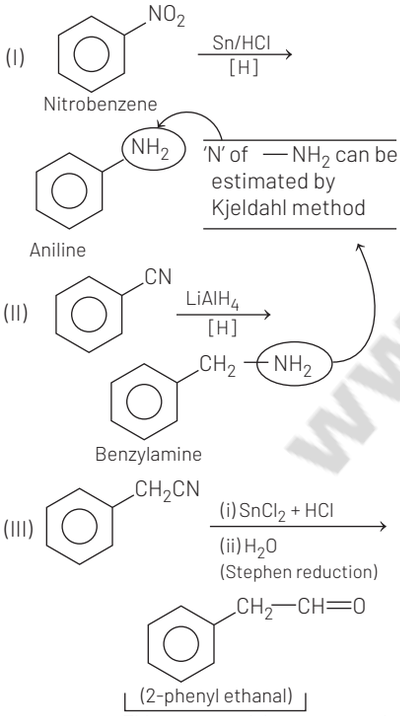
[2020, 3 Sep Shift-I]

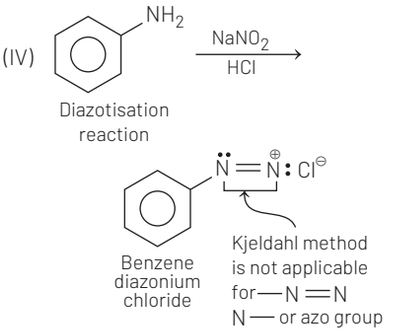


(a) III and IV (b) I and IV (c) I, III and IV (d) II and III

Ans. ***(a)***

Complete reactions I, II, III, IV are as follows :





So, products of reactions (c) and (d) (option-a) fail to give Kjeldahl's method. So, option (a) is correct.

05 The correct match between Item I and Item II is

	Item I		Item II
A.	Ester test	P.	Tyr
B.	Carbylamine test	Q.	Asp
C.	Phthalein dye test	R.	Ser
		S.	Lys

[2019, 11 Jan Shift-II]

(a) A → Q; B → S; C → R

(b) A → R, B → Q; C → P

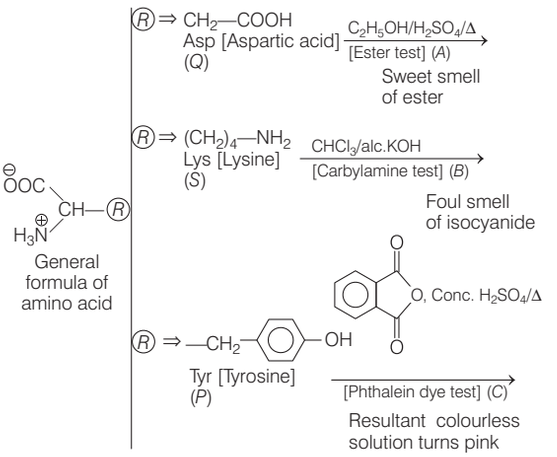
(c) A → R; B → S; C → Q

(d) A → Q; B → S; C → P

Ans. ***(d)***

The correct match is :

A → (Q); (B) → (S) (C) → (P)



(A) Ester test confirms the presence of —COOH group.

(B) Carbylamine test confirms the presence of $-NH_2$ group (1°).

(C) Phthalein dye test confirms the presence of phenolic —OH group.

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TOPIC 2
Chemistry Involved in Organic and Inorganic Compounds

06 An inorganic compound '*X*' on treatment with concentrated H_2SO_4 produces brown fumes and gives dark brown ring with $FeSO_4$ in presence of concentrated H_2SO_4. Also compound '*X*' gives precipitate '*Y*', when its solution in dilute HCl is treated with H_2S gas. The precipitate '*Y*' on treatment with concentrated HNO_3 followed by excess of NH_4OH further gives deep blue coloured solution, compound '*X*' is **[2021, 20 July Shift-I]**

(a) $Co(NO_3)_2$ (b) $P(NO_2)_2$
(c) $Cu(NO_3)_2$ (d) $Pb(NO_3)_2$

Ans. ***(c)***

Compound '*X*' is copper nitrate, i.e. $Cu(NO_3)_2$ is an inorganic compound. On treatment with concentrated H_2SO_4 produces brown fumes and gives dark brown ring with $FeSO_4$ in presence of concentrated H_2SO_4. Chemical reaction is as follows

$$\underset{X}{NO_3^-}\ (\text{Anion}) + \underset{(\text{Conc.})}{H_2SO_4} \longrightarrow \underset{(\text{Brown fumes})}{NO_2\uparrow} + H_2O$$

$$\underset{(\text{Sol})}{FeSO_4} + \underset{(\text{Conc.})}{H_2SO_4} + \underset{X}{NO_3^-} \longrightarrow \underset{(\text{Dark brown})}{[Fe(H_2O)_5(NO)]}$$

Cu^{2+} is a group II cation with group II reagents (HCl/H_2S), it gives black coloured precipitates. These precipitates gives blue colour solution on treatment with HNO_3 followed by excess of NH_4OH.

$$\underset{X}{Cu^{2+}}\ (\text{Cation}) + \underset{(\text{Group II, reagent})}{(\text{Dil HCl} + H_2S)} \longrightarrow \underset{Y}{CuS\downarrow}\ (\text{Black ppt.})$$

$$\underset{Y}{CuS} \xrightarrow{\text{Conc. } HNO_3} \underset{X}{Cu(NO_3)_2} + NO_2 + H_2SO_4 + H_2O \quad (\text{Soluble})$$

$$\xrightarrow{\text{Excess } NH_4OH \text{ sol.}} \underset{(\text{Deep blue colour})}{[Cu(NH_3)_2]^{2+}}$$

$\therefore$ $X \longrightarrow \underset{\text{Copper nitrate}}{Cu(NO_3)_2}$

07 Match List-I with List-II.

	List-I (Test / Reagents / Observation(s))		List-II (Species detected)
A.	Lassaigne's test	(i)	Carbon
B.	Cu(II) oxide	(ii)	Sulphur
C.	Silver nitrate	(iii)	N, S, P, and halogen
D.	The sodium fusion extract gives black precipitate with acetic acid and lead acetate	(iv)	Halogen specifically

The correct match is **[2021, 16 March Shift-II]**

(a) A-(iii), B-(i), C-(ii), D-(iv)
(b) A-(i), B-(iv), C-(iii), D-(ii)
(c) A-(iii), B-(i), C-(iv), D-(ii)
(d) A-(i), B-(ii), C-(iv), D-(iii)

Ans. ***(c)***

(A) Lassaigne test is used to detect N, S, P, *X* elements.
The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place.

$$Na + C + N \xrightarrow{\Delta} NaCN$$
$$2Na + S \xrightarrow{\Delta} Na_2S$$
$$Na + X \xrightarrow{\Delta} NaX \quad (X = Cl, Br \text{ or } I)$$

(B) Carbon and hydrogen are detected by heating the compound with copper (II) oxide.

$$C + 2CuO \longrightarrow 2Cu + CO_2$$
$$2H + CuO \longrightarrow Cu + H_2O$$

(C) Halides are detected by silver nitrate.
They form precipitate of Ag*X* except fluorine.
$Ag^+(aq) + X^-(aq) \longrightarrow AgX(s)$

(D) Sodium fusion extract gives black precipitate of PbS with acetic acid and lead acetate to confirm the presence of sulphur.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3COONa$$

08 Seliwanoff test and xanthoproteic test are used for the identification of ..... and ..... respectively. **[2021, 26 Feb Shift-II]**

(a) aldoses, ketoses (b) proteins, ketoses
(c) ketoses, proteins (d) ketoses, aldoses

Ans. ***(c)***

Seliwanoff and xanthoproteic tests are used for the identification of ketoses and proteins respectively.

Seliwanoff test It is a chemical test which distingusihes between aldose sugars (e.g. glucose and maltose) and ketose sugars (e.g., fructose and sucrose). The test is based on the principle that, when heated with acid, ketoses are more readily dehydrated than aldoses. The reagents used in the test consist of conc. HCl and resorcinol.

For ketoses, a deep cherry red colour is formed rapidly indicating a positive test.

Xanthoproteic test It is qualitative test to detect the presence of protein soluble in a solution using HNO_3.

In this test, solution of protein is first heated with conc. HNO_3 and then the mixture is neutralised by 40% NaOH solution. If the colour changes from yellow to orange, this confirms presence of a protein.

Protein solution $\xrightarrow[\text{(ii) 40\%NaOH}]{\text{(i) Conc. } HNO_3/\Delta}$ Yellow colouration which finally changes into orange colour.

09 Which of the following is a false statement?

(a) Carius tube is used in the estimation of sulphur in an organic compound **[2021, 26 Feb Shift-I]**
(b) Carius method is used for the estimation of nitrogen in an organic compound
(c) Phosphoric acid produced on oxidation of phosphorus present in an organic compound is precipitated as $Mg_2P_2O_7$ by adding magnesia mixture
(d) Kjeldahl's method is used for the estimation of nitrogen in an organic compound

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Ans. ***(b)***

Statement (b) is false whereas all other statements are true.

There are two methods for estimation of nitrogen in an organic compound which are Duma's method and Kjeldahl's method.

So, the statement in option (b) is false.

10 Which of the following compound is added to the sodium extract before addition of silver nitrate for testing of halogens? **[2021, 25 Feb Shift-II]**

(a) Hydrochloric acid (b) Sodium hydroxide

(c) Nitric acid (d) Ammonia

Ans. ***(c)***

Nitric acid is added to sodium extract before addition of silver nitrate for testing halogens. Because it decomposes NaCN and Na_2S or else they interfere in the test.

The reaction are as follows :

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$\underset{\text{Sodium extract}}{Na_2S} + \underset{\text{Nitric acid}}{HNO_3} \longrightarrow NaNO_3 + H_2S\uparrow$$

11 On heating compound (*A*) gives a gas (*B*) which is a constituent of air. This gas when treated with H_2 in the presence of a catalyst gives another gas (*C*) which is basic in nature.

(*A*) should not be **[2020, 2 Sep Shift-I]**

(a) NH_4NO_2 (b) $(NH_4)_2Cr_2O_7$

(c) NaN_3 (d) $Pb(NO_3)_2$

Ans. ***(d)***

(*A*) can be NH_4NO_2 or $(NH_4)_2Cr_2O_7$ or NaN_3 but not $Pb(NO_3)_2$ because each option a, b, c on heating liberates N_2 gas (*B*).

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

$$2NaN_3 \xrightarrow{\Delta} 3N_2 + 2Na$$

But, $Pb(NO_3)_2$ on heating liberates NO_2 and O_2.

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$$

N_2 is a constituent of air (N_2 = 78%, O_2 = 21% by volume). It reacts with H_2 in presence of a catalyst to give ammonia NH_3(*C*) gas which is basic in nature.

$$N_2 + 3H_2 \xrightarrow[Fe\,(catalyst)]{200\ atm,\ 773\ K} 2NH_3$$

12 If you spill a chemical toilet cleaning liquid on your hand, your first aid would be **[2020, 2 Sep Shift-II]**

(a) vinegar (b) aqueous NaOH

(c) aqueous $NaHCO_3$ (d) aqueous NH_3

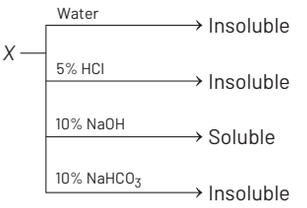
Ans. ***(c)***

Toilet cleaning liquid contains mainly HCl and surfactants like classical ATX. HCl is corrosive to our skin. So, it should be removed immediately.

The first aid for removal of HCl should be basic in nature. But NaOH is a hard base whereas NH_4OH is a very soft base. So, the best substance to remove the spill (HCl) is $NaHCO_3$.

$$HCl + NaHCO_3 \longrightarrow NaCl + CO_2\uparrow + H_2O$$

13 An organic compound *X* showing the following solubility profile is **[2019, 8 April Shift-I]**

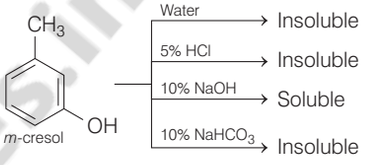


(a) *o*-toluidine (b) oleic acid

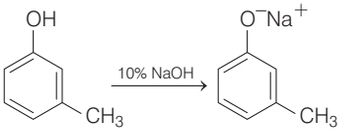
(c) *m*-cresol (d) benzamide

Ans. ***(c)***

m-cresol is the organic compound that shows the following solubility profile.



m-cresol on reaction with 10% NaOH forms 3-methyl sodiumphenoxide ion.



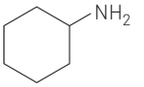
It does not react with H_2O, 5% HCl and 10% $NaHCO_3$.

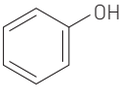
Oleic acid ($C_{18}H_{34}O_2$) is soluble in 10% NaOH and 10% $NaHCO_3$ due to the presence of COOH group.

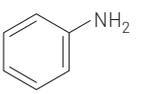
Benzamide ($C_6H_5\overset{\overset{O}{\|}}{C}NH_2$) is insoluble in 5% HCl, 10% NaOH and 10% $NaHCO_3$ due to the presence —$CONH_2$ group. o-toluidine is soluble in 5%. HCl due to presence of basic group (—NH_2) attached to ring.

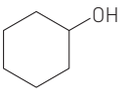
14 The organic compound that gives following qualitative analysis is **[2019, 9 April Shift-I]**

Test	**Inference**
(i) Dil. HCl	Insoluble
(ii) NaOH solution	Soluble
(iii) Br_2 /water	Decolourisation

(a) 

(b) 

(c) 

(d) 

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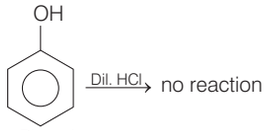
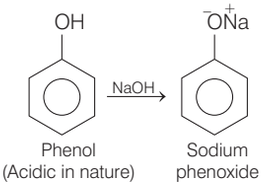
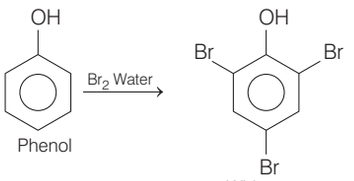
Ans. ***(b)***

Phenol (ArOH) is insoluble in dil. HCl and readily soluble in NaOH solution. It reacts with Br_2/water to give 2, 4, 6-tribromophenol. It readily decolourises the yellow colour of Br_2 water. Reactions involved are as follows :

- 

- 

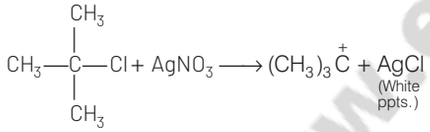
- 

15 Which one of the following is likely to give a precipitate with $AgNO_3$ solution? **[2019, 9 April Shift-II]**

(a) $CH_2 = CH-Cl$ (b) CCl_4
(c) $CHCl_3$ (d) $(CH_3)_3CCl$

Ans. ***(d)***

$(CH_3)_3CCl$ gives a precipitate with $AgNO_3$ solution because it forms stable carbocation. (i.e. tertiary) that readily combines with $AgNO_3$ to give precipitates of AgCl.



$CH_2 = CH-Cl$ forms unstable carbocation.

Hence, it does not readily react with $AgNO_3$.

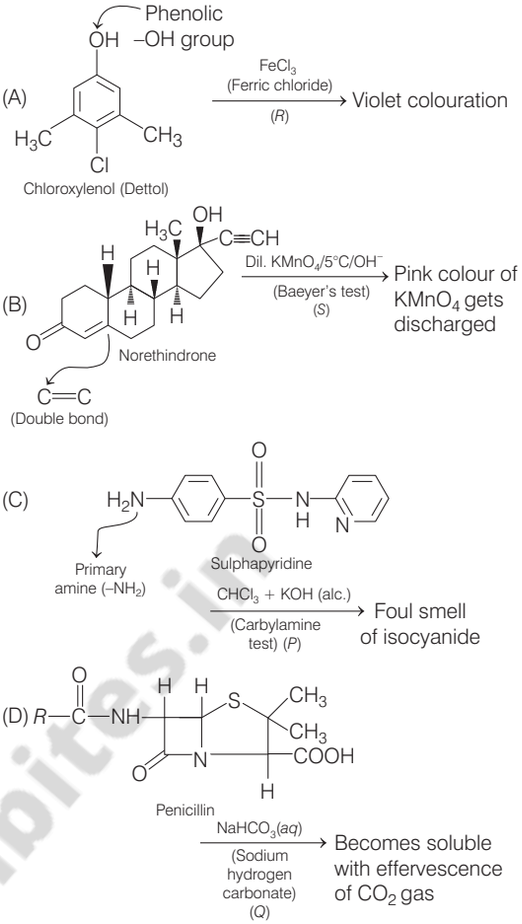
16 The correct match between Item-I and Item-II is

	Item-I (Drug)		**Item- II** (Test)
A.	Chloroxylenol	P.	Carbylamine test
B.	Norethindrone	Q.	Sodium hydrogen carbonate test
C.	Sulphapyridine	R.	Ferric chloride test
D.	Penicillin	S.	Bayer's test

[2019, 9 Jan Shift-I]

(a) A → R ; B → P ; C → S ; D → Q
(b) A → R ; B → S ; C → P ; D → Q
(c) A → Q ; B → P ; C → S ; D → R
(d) A → Q ; B → S ; C → P ; D → R

Ans. ***(b)***



Thus, the correct match is :

A → R; B → S; C → P; D → Q

17 The correct match between item 'I' and item 'II' is

	Item 'I' (Compound)		**Item 'II'** (Reagent)
(A)	Lysine	(P)	1-naphthol
(B)	Furfural	(Q)	Ninhydrin
(C)	Benzyl alcohol	(R)	$KMnO_4$
(D)	Styrene	(S)	Ceric ammonium nitrate

[2019, 10 Jan Shift-II]

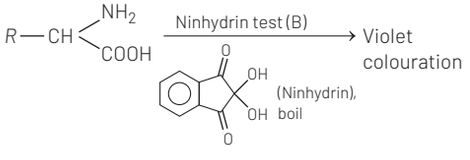
Codes

	A	B	C	D		A	B	C	D
(a)	Q	R	S	P	(b)	R	P	Q	S
(c)	Q	P	S	R	(d)	Q	P	R	S

Ans. ***(c)***

(A) → Q; B → (P) ; C → (S), D → (R)

(A) Lysine (R=-$(CH_2)_4$-NH_2)



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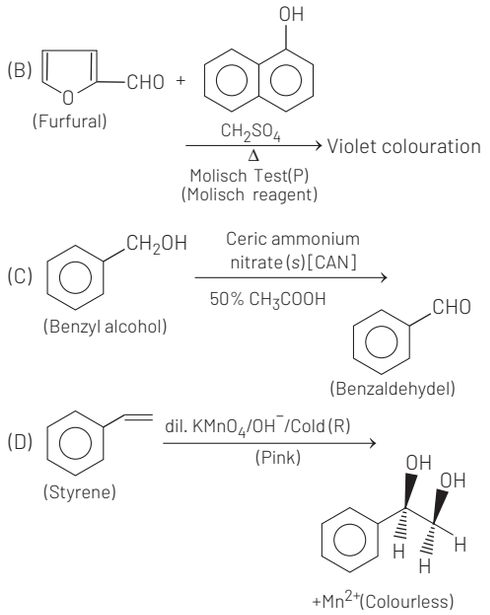

18 The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is

[AIEEE 2004]

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Na_3[Fe(CN)_6]$

(c) $Fe(CN)_3$ (d) $Na_4[Fe(CN)_5NOS]$

Ans. ***(a)***

If nitrogen is present in organic compound, then sodium extract contains NaCN.

$$Na + C + N \xrightarrow{Fuse} NaCN$$

$$FeSO_4 + 6NaCN \longrightarrow \underset{(A)}{Na_4[Fe(CN)_6]} + Na_2SO_4$$

A changes to Prussian blue $Fe_4[Fe(CN)_6]_3$ on reaction with $FeCl_3$.

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

TOPIC 3
Chemistry Involved in Titrimetric Exercise

19 When 10 mL of an aqueous solution of $KMnO_4$ was titrated in acidic medium, equal volume of 0.1 M of an aqueous solution of ferrous sulphate was required for complete discharge of colour.

The strength of $KMnO_4$ in g/L is

..... $\times 10^{-2}$. (Nearest integer)

[Atomic mass of K = 39, Mn = 55, O = 16]

[2021, 27 Aug Shift-I]

Ans. ***(316)***

Let molarity of $KMnO_4 = x$

$$KMnO_4 + FeSO_4 \longrightarrow Fe(SO_4)_3 + Mn^{2+}$$
$$n = 5 \qquad n = 1$$

(Equivalent of $KMnO_4$ reacted) = (Equivalent of $FeSO_4$ reacted)

$\Rightarrow$ $5x \times 10 = 1 \times 0.1 \times 10$

$x = 0.02$ M

Molar mass of $KMnO_4 = 158$ g / mol

Strength $= x \times 158 = 0.02 \times 158 = 3.16$ g / L

$= 316 \times 10^{-2}$ g /L

$\therefore$ $x \approx 316$.

20 The OH^- concentration in a mixture of 5.0 mL of 0.0504 M NH_4Cl and 2 mL of 0.0210 M NH_3 solution is $x \times 10^{-6}$ M. The value of *x* is ..... . (Nearest integer)

[Given, $K_w = 1 \times 10^{-14}$ and $K_b = 1.8 \times 10^{-5}$]

[2021, 26 Aug Shift-I]

Ans. ***(3)***

Number of moles of NH_4Cl = concentration of $NH_4Cl \times$ volume of NH_4Cl

$= 0.0504\ M \times 5\ mL = 0.2520$ millimoles

Total volume of solution in mixture

= Volume of NH_4Cl solution + volume of NH_3 solution

$= 5 + 2 = 7$ mL.

Concentration of NH_4Cl in mixture

$$= \frac{\text{Number of moles of } NH_4Cl}{\text{Total volume}}$$

$$= \frac{0.2520 \text{ millimole}}{7 \text{ mL}} = 0.036 \text{ M}$$

Number of moles of NH_3 = concentration of $NH_3 \times$ volume of NH_3

$= 0.0210 \times 2 = 0.042$ millimole

$$\text{Concentration of } NH_3 \text{ in mixture} = \frac{\text{Number of moles of } NH_3}{\text{Total volume}}$$

$$= \frac{0.042}{7} = 0.006 \text{ M}$$

According to Handerson's equation

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$[Salt] = [NH_4Cl]$

$[Base] = [NH_3]$

$$pOH = -\log K_b + \log \frac{0.036}{0.006}$$

$$pOH = -\log(1.8 \times 10^{-5}) + 0.7782$$

$$pOH = 5.523$$

$\because$ $pOH = -\log[OH^-]$

So, $[OH^-] = 2.9 \times 10^{-6} \approx 3 \times 10^{-6}$

$\therefore$ $x = 3$

21 Given below are two statements.

Statement I In the titration between strong acid and weak base methyl orange is suitable as an indicator.

Statement II For titration of acetic acid with NaOH phenolphthalein is not a suitable indicator.

In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 26 Aug Shift-I]

(a) Statement I is false but statement II is true.

(b) Statement I is true but statement II is false.

(c) Both statement I and statement II are true.

(d) Both statement I and statement II are false.

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Ans. ***(b)***

In the titration of strong acid with the weak base methyl orange is an suitable indicator. Initially, pH of weak base is high, as acid is added pH falls slowly and equivalence point is attained. (Equivalence point is point when chemical equivalent quantities of acid and base are mixed). After equivalence point pH falls sharply. So, methyl orange having pH range 3.2 - 4.4 will work as suitable indicator. Methyl orange shows red colour in acidic medium and yellow colour in basic medium.

Hence, statement I is true.

In titration of weak acid and strong base initially pH of weak acid is below 7. As strong base is added pH increases slowly and equivalence point is attained. After equivalence point pH abruptly increases. So, phenolphthalein having pH range 8.2–10.0 will work as suitable indicator. Phenolphthalein is colourless in acidic solution whereas pink in basic solution.

Hence, statement II is false.

22 Consider titration of NaOH solution *versus* 1.25 M oxalic acid solution. At the end point following burette readings were obtained.

(i) 4.5 mL (ii) 4.5 mL (iii) 4.4 mL
(iv) 4.4 mL (v) 4.4 mL

If the volume of oxalic acid taken was 10.0 mL, then the molarity of the NaOH solution is ..... M. (Rounded off to the nearest integer) **[2021, 25 Feb Shift-II]**

Ans. ***(6)***

Average burette reading = Volume of NaOH solution (V_1)

$$= \frac{4.5 + 4.5 + 4.4 + 4.4 + 4.4}{5}$$

$$= 4.44 \text{ mL}$$

Strength of NaOH solution = S_1(M) (say) = S_1(N)

Volume of oxalic acid solution (V_2) = 10 mL

Strength of oxalic acid solution (S_2) = 1.25 M 3= 1.25×2 N

So, $V_1S_1 = V_2S_2$ ($\because$ Law of equivalence)

$$\Rightarrow \quad S_1 = \frac{V_2S_2}{V_1} = \frac{10 \times (1.25 \times 2)}{4.44} = 5.63 \text{ N}$$

$$\simeq 6 \text{ M} = 6 \text{ M}$$

Note n-factor of NaOH = 1

n-factor of $H_2C_2O_4$ = 2 (oxalic acid)

$$N = M \times n$$

23 0.4 g mixture of NaOH, Na_2CO_3 and some inert impurities was first titrated with $\frac{N}{10}$ HCl using phenolphthalein as an indicator, 17.5 mL of HCl was required at the end point. After this methyl orange was added and titrated. 1.5 mL of same HCl was required for the next end point. The weight percentage of Na_2CO_3 in the mixture is ..... (Rounded off to the nearest integer). **[2021, 25 Feb Shift-I]**

Ans. ***(4)***

As given, NaOH and Na_2CO_3 is titrated with N/10 HCl.

For NaOH,

Equivalents of NaOH = Equivalents of HCl

Equivalents of HCl = Normality × Volume (L)

$$= 0.1 \times \frac{17.5}{1000}$$

Equivalent of HCl = 1.75×10^{-3}

Equivalents of NaOH = 1.75×10^{-3}

Weight of NaOH = Equivalent of NaOH × equivalent weight of NaOH

$$= 40 \times 1.75 \times 10^{-3} = 0.07 \text{ g}$$

Now, weight % of NaOH

$$= \frac{0.07}{0.4} \times 100 = \frac{70}{4} = 17.5\%$$

Similarly for Na_2CO_3,

Equivalent of HCl = Equivalent of Na_2CO_3

Equivalent of $Na_2CO_3 = 0.1 \times \frac{1.5}{1000} = 0.15 \times 10^{-3}$

Weight of Na_2CO_3 = Equivalent of Na_2CO_3 × equivalent weight of Na_2CO_3

$$= 0.15 \times 10^{-3} \times 106 = 15.9 \times 10^{-3} \text{ g}$$

Weight % of $Na_2CO_3 = \frac{15.9 \times 10^{-3}}{0.4} \times 100$

$$= 0.039 \times 100 = 3.9\% \simeq 4\%$$

24 While titrating dilute HCl solution with aqueous NaOH, which of the following will not be required?

(a) Pipette and distilled water **[2020, 2 Sep Shift-I]**
(b) Burette and porcelain tile
(c) Bunsen burner and measuring cylinder
(d) Clamp and phenolphthalein

Ans. ***(c)***

Titration (neutralisation) of dil. HCl solution with aqueous NaOH will require the following steps and apparatus. NaOH solution made with distilled water and solid NaOH is taken in a burette and then it is fitted with a clamp.

A given volume of standard HCl solution (dilute) is then pipetted out and taken in a conical flask for titration. Then, few drops of phenolphthalein indicator is added in this HCl solution. So, we do not require measuring cylinder and bunsen burner as the titration takes place at room temperature.

25 The volume strength of 8.9 M H_2O_2 solution calculated at 273 K and 1 atm is ..... . ($R = 0.0821$ L atm K^{-1} mol^{-1}) (rounded off to the nearest integer). **[2020, 3 Sep Shift-I]**

Ans. ***(100.00)***

$$\text{"x vol" } H_2O_2 = \frac{x}{11.2} \text{ M } H_2O_2$$

So, $\frac{x}{11.2} = 8.9$

$$\Rightarrow \quad x = 11.2 \times 8.9 = 99.68 \simeq 100$$

So, at NTP volume strength of 8.9 M H_2O_2 solution is 100 vol.

26 A 20.0 mL solution containing 0.2g impure H_2O_2 reacts completely with 0.316 g of $KMnO_4$ in acid solution. The purity of H_2O_2 (in%) is ..... (molecular weight of H_2O_2 = 34; molecular weight of $KMnO_4$ = 158). **[2020, 4 Sep Shift-I]**

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Ans. ***(85)***

Given, volume of solution = 20.0 mL

Impure sample of H_2O_2 = 0.2 g

Mass of $KMnO_4$ = 0.316 g

Impure H_2O_2 react with $KMnO_4$ (acidic)

$$\overset{+7}{K}\overset{+7}{Mn}O_4 + \overset{-1}{H_2O_2} \longrightarrow \overset{+2}{Mn} + \overset{0}{O_2}$$

$KMnO_4$ acts as an oxidising agent,

$$\overset{+7}{Mn} + 5e^- \longrightarrow \overset{+2}{Mn}$$

(valency factor = 5)

$$\overset{-1}{O_2} \longrightarrow \overset{0}{O_2} + 2e^-$$

(valency factor = 2)

We have to compare both $KMnO_4$ and H_2O_2.

$$(\text{Mass equivalent})_{H_2O_2} = (\text{Mass equivalent})_{KMnO_4}$$

$$\frac{\text{Weight}}{\text{molecular weight/valence factor}} \times 1000$$

$$= \frac{\text{weight}}{\text{molecular weight/valence factor}} \times 1000$$

$$\frac{(\text{weight})_{H_2O_2}}{34/2} \times 1000 = \frac{0.316}{158/5} \times 1000$$

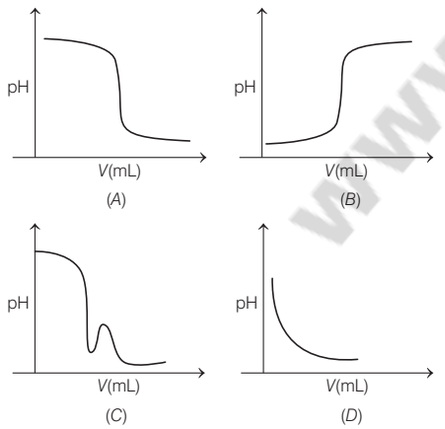
$$(\text{weight})_{H_2O_2} = \frac{0.316}{158} \times 5 \times \frac{34}{2} = \frac{26.86}{158}$$

$$(\text{weight})_{H_2O_2} = 0.17 \text{ g}$$

$$(\text{Purify})_{H_2O_2} = \frac{(\text{Pure})_{H_2O_2}}{(\text{Impure})_{H_2O_2}} \times 100 = \frac{0.17}{0.2} \times 100 = 85\%$$

27 In an acid-base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment?

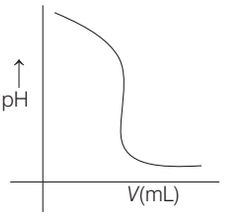
[2019, 9 April Shift-II]



(a) (*D*) (b) (*A*) (c) (*B*) (d) (*C*)

Ans. ***(b)***

The graph that shows the correct change of pH of the titration mixture in the experiment is



In this case, both the titrants are completely ionised.

$$HCl + NaOH \rightleftharpoons \overset{+}{Na}\overset{-}{Cl} + H_2O$$

As $\overset{\oplus}{H}$ is added to a basic solution, $[OH^{\ominus}]$ decreases and $[H^+]$ increases. Therefore, pH goes on decreasing. As the equivalence point is reached, $[OH^{\ominus}]$ is rapidly reduced. After this point $[OH^{\ominus}]$ decreases rapidly and pH of the solution remains fairly constant. Thus, there is an inflexion point at the equivalence point.

The difference in the volume of NaOH solution between the end point and the equivalence point is not significant for most of the commonly used indicators as there is a large change in the pH value around the equivalence point. Most of them change their colour across this pH change.

28 25 mL of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution?

[2019, 11 Jan Shift-II]

(a) 75 mL (b) 25 mL
(c) 12.5 mL (d) 50 mL

Ans. ***(b)***

The reaction of HCl with Na_2CO_3 is as follows:

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$$

We know that, M_{eq} of HCl = M_{eq} of Na_2CO_3

$$\frac{25}{1000} \times 1 \times M_{HCl} = \frac{30}{1000} \times 0.1 \times 2$$

$$M_{HCl} = \frac{30 \times 0.2}{25} = \frac{6}{25} \text{ M}$$

The reaction of HCl with NaOH is as follows:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Also, M_{eq} of HCl = M_{eq} of NaOH

$$\frac{6}{25} \times 1 \times \frac{V}{1000} = \frac{30}{1000} \times 0.2 \times 1$$

$$V = 25 \text{ mL}$$

29 50 mL of 0.5 M oxalic acid is needed to neutralise 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is

[2019, 12 Jan Shift-I]

(a) 40 g (b) 80 g (c) 20 g (d) 10 g

Ans. ***(*)***

The reaction takes place as follows,

$$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$$

Now, 50 mL of 0.5 M $H_2C_2O_4$ is needed to neutralize 25 mL of NaOH.

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$\therefore$ Meq of $H_2C_2O_4$ = Meq of NaOH

$$50 \times 0.5 \times 2 = 25 \times M_{NaOH} \times 1$$

$$M_{NaOH} = 2M$$

Now, $$\text{molarity} = \frac{\text{Number of moles}}{\text{Volume of solution (in L)}}$$

$$= \frac{\text{Weight/molecular mass}}{\text{Volume of solution (in L)}}$$

$$2 = \frac{w_{NaOH}}{40} \times \frac{1000}{50}$$

$$w_{NaOH} = \frac{2 \times 40 \times 50}{1000} = 4g$$

Thus, (*) none option is correct.

30 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1M HCl solution. The excess of the acid required 15 ML of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is **[AIEEE 2010]**

(a) 59.0 (b) 47.4 (c) 23.7 (d) 29.5

Ans. ***(c)***

Mass of organic compound = 29.5 mg

mmoles of HCl = $20 \times 0.1 = 2$ mmoles

mmoles of NaOH = $15 \times 0.1 = 1.5$ mmole

Involved reactions are

$$NH_3 + \underset{\substack{\text{(2 mmoles}\\ \text{initially taken)}}}{HCl} \longrightarrow NH_4Cl$$

$$\underset{\text{(Lewis acid)}}{HCl} + \underset{\substack{\text{(1.5 mmoles}\\ \text{initially taken)}}}{NaOH} \longrightarrow NaCl + H_2O$$

From the above equation, it is clear that

mmoles of HCl reacted with NaOH = 2 – 1.5 = 0.5 mmol

m moles of NH_3 reacted in first equation with HCl = 0.5×17 mg

Mass of $NH_3 = 0.5 \times 17$ mg = 8.5 mg

Mass of N contained in $NH_3 = 8.5\text{ mg} \times \frac{14}{17} = 7$ mg

Thus, % of N present in OC $= \frac{7}{29.5} \times 100 = 23.7\%$

TOPIC 4
Qualitative Salt Analysis

31 To an aqueous solution containing ions such as Al^{3+}, Zn^{2+}, Ca^{2+}, Fe^{3+}, Ni^{2+}, Ba^{2+} and Cu^{2+} conc. HCl, was added followed by H_2S. The total number of cations precipitated during this reaction is/are **[2021, 27 July Shift-II]**

(a) 1 (b) 3 (b) 4 (d) 2

Ans. ***(a)***

Only Cu^{2+} get precipitated when HCl followed by H_2S was added. Al^{3+} and Fe^{3+} sulphides hydrolyse in water. Ni^{2+} and Zn^{2+} require basic medium with H_2S to form ppt. Ca^{2+} and Ba^{2+} sulphides are soluble.

Hence, we will recieve ppt. of only CuS.

32 Which one of the following set of elements can be detected using sodium fusion extract ? **[2021, 27 July Shift-II]**

(a) Sulphur, nitrogen, phosphorus, halogens
(b) Phosphorus, oxygen, nitrogen, halogens
(c) Nitrogen, phosphorus, carbon, sulphur
(d) Halogens, nitrogen, oxygen, sulphur

Ans. ***(a)***

By sodium fusion extract we can detect sulphur, nitrogen, phosphorus and halogens. The elements present in the compound are converted from covalent into ionic form by fusing the compound with sodium metal. Following reactions take place :

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX\ (X = Cl, Br \text{ or } I)$$

$$3Na + PO_4^{3-} \xrightarrow{\Delta} Na_3PO_4$$

33 In Tollen's test for aldehyde, the overall number of electron(s) transferred to the Tollen's reagent formula $[Ag(NH_3)_2]^+$ per aldehyde group to form silver mirror is ..... (Round off to the nearest integer). **[2021, 18 March Shift-II]**

Ans. ***(2)***

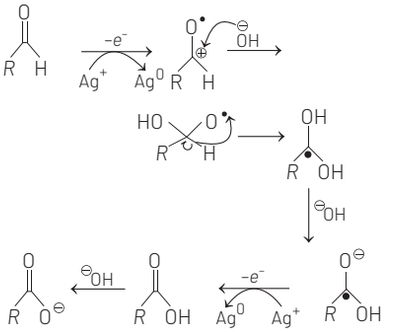
When an aldehyde is heated with freshly prepared Tollen's reagent i.e. $[Ag(NH_3)_2]^+$, a bright silver mirror of Ag is formed.

$$AgNO_3 + NaOH \longrightarrow AgOH + NaNO_3$$

$$2AgOH \longrightarrow Ag_2O + H_2O$$

$$Ag_2O + 4NH_3 + H_2O \longrightarrow \underset{\text{Tollen's reagent}}{2Ag(NH_3)_2^+} + 2OH^-$$

Reaction of aldehyde with Tollen's reagent take place as follows



Total $2e^-$ transfer to Tollen's reagent.

34. If Fe^{3+} and Cr^{3+} both are present in group III of qualitative analysis, then distinction can be made by **[AIEEE 2002]**

(a) addition of NH_4OH in the presence of NH_4Cl when only $Fe(OH)_3$ is precipitated

(b) addition of NH_4OH in presence of NH_4Cl when $Cr(OH)_3$ and $Fe(OH)_3$ both are precipitated and on adding Br_2 water and NaOH, $Cr(OH)_3$ dissolves

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(c) precipitate of $Cr(OH)_3$ and $Fe(OH)_3$ as obtained in (b) are treated with conc. HCl when only $Fe(OH)_3$ dissolves

(d) both (b) and (c)

Ans. ***(b)***

If Fe^{3+} and Cr^{3+} both are present, then very first solid ammonium chloride and ammonium hydroxide is added slowly till the solution smells of ammonia. Fe^{3+} and Cr^{3+} precipitates in the hydroxide form.

For identification, precipitate is treated with NaOH and Br_2 water, yellow colouration confirms Cr^{3+} ion.

$$2NaOH + Br_2 \longrightarrow NaBrO + NaBr + H_2O$$

$$NaBrO \longrightarrow NaBr + [O]$$

$$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow 2Na_2CrO_4 + 5H_2O$$

Solution is acidified and treated with lead acetate solution.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{(Yellow ppt)}}{PbCrO_4} + 2CH_3COONa$$

TOPIC 5
Experiments Involving Enthalpy

35 When silver nitrate solution is added to potassium iodide solution then the sol produced is

[2021, 22 July Shift-II]

(a) AgI/I^- (b) AgI/Ag^+

(c) KI/NO_3^- (d) $AgNO_3/NO_3^-$

Ans. ***(a)***

Since, $AgNO_3$ solution was passed to KI solution, the AgI/I^- sol was produced. (Here, the KI solution through which $AgNO_3$ passed, was considered to be in excess).

As we know that, colloids can be prepared from precipitate by using suitable electrolytes. Colloids may be positively or negatively charged depend on electrolyte we adding.

If we add $AgNO_3$ and KI, it gives AgI and KNO_3.

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

and thus AgI adsorb I^- ion as KI is in excess.

If KNO_3 added, then $AgNO_3$ will be in excess, so

AgI adsorb Ag^+ ion.

Hence, AgI produce the I^- ion.

36 The reaction of cyanamide, $NH_2CN(s)$ with oxygen was run in a bomb calorimeter and ΔU was found to be $-742.24\ kJ\ mol^{-1}$. The magnitude of ΔH_{298} for the reaction

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + O_2(g) + H_2O(l)$$

is ..... kJ (Rounded off to the nearest integer).

[Assume ideal gases and $R = 8.314\ J\ mol^{-1}\ K^{-1}$]

[2021, 25 Feb Shift-I]

Ans. ***(741)***

$$\Delta U = -742.24\ kJ\ mol^{-1}$$

Δn_g = [Number of gaseous molecules of products – Number of gaseous molecules of reactants]

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + O_2(g) + H_2O(l)$$

$$\Delta n_g = 2 - \frac{3}{2} = \frac{1}{2}$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$= -742.24 + \frac{1}{2} \times \frac{8.314}{1000} \times 298 = -741\ kJ/mol$$

Hence, answer is 741.

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