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Chemistry for Engineers

Dr. Mira Das
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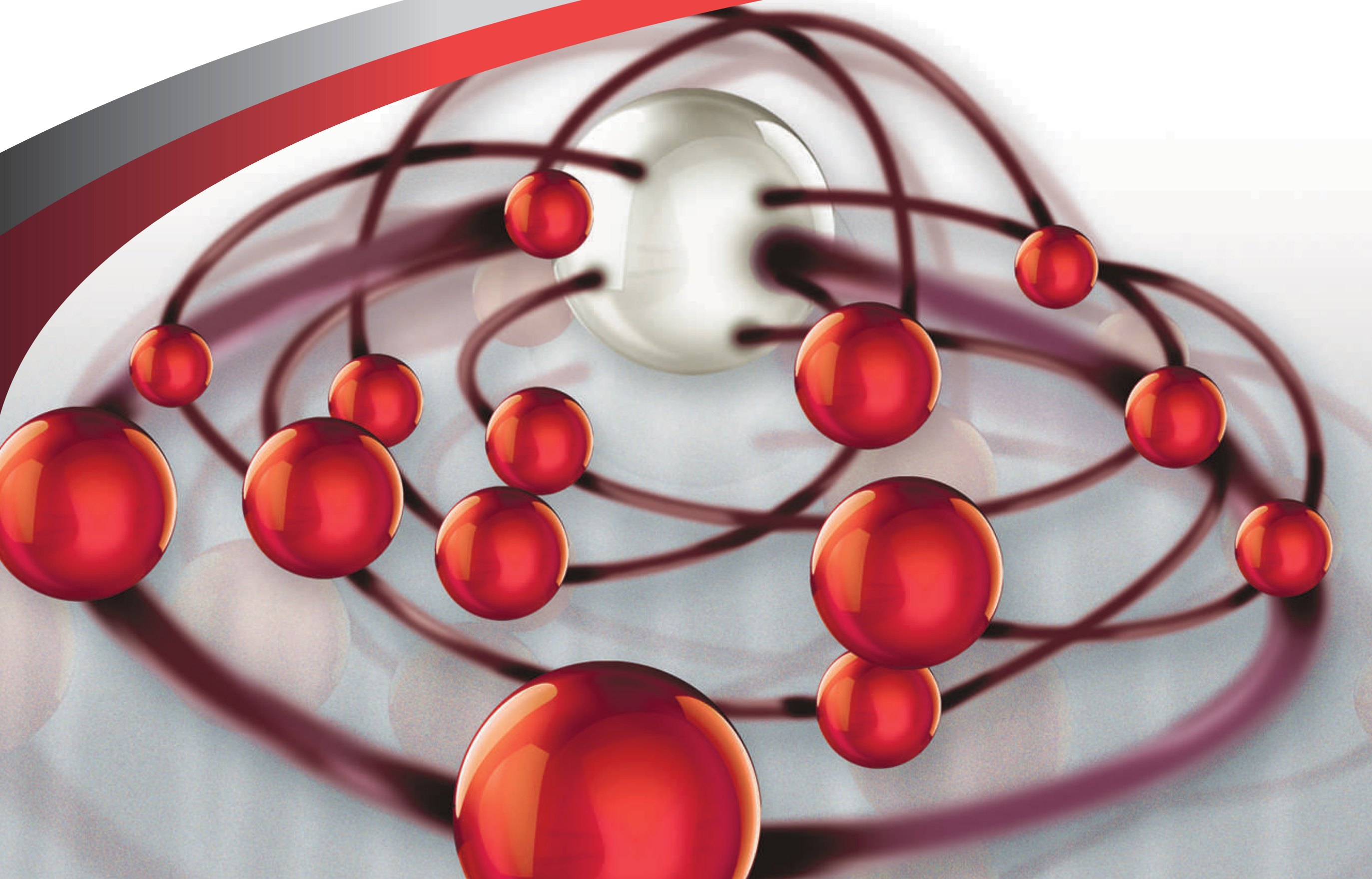

Chemistry
for Engineers

A Textbook for B. Tech. students of
Biju Patnaik University of Technology (BPUT), Odisha
Siksha 'O' Anusandhan University (S'O'A), Odisha
and Other Indian Technical Universities

Chemistry for Engineers

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PREFACE

There is chemistry in each piece of finely engineered product that we use at home and in industry. The undergraduate students of engineering in all branches need to negotiate their understanding of the working of scientific principles at work. Here comes the theory and application of chemistry in industries which is crucial for sustainable progress. All emerging branches of engineering are specialized today and accordingly the scope of chemistry is expanding in different directions. The dramatic changes in engineering and technology are possible because chemistry develops the atomic structure and equilibrium of what is required. The first year students of engineering need to know clearly the fundamental concepts of chemistry and test the efficacy of their applications in engineering and to see how chemistry is an invisible process beneath the visible technology. This book is also an attempt to straighten out the guises of assumption which engineering students often harbor in their mind, that is, chemistry is an ancillary subject to the syllabi of engineering. In reality it is chemistry which takes the students to the core of engineering and technology. The study of spectroscopy helps to do mapping of surface, multiplex scanning and depth profile of materials. It further helps to create new chemical composites which have varied applications, in a wide range of products from television sets to components in spacecrafts as well. Similarly coordination chemistry helps us to understand the uses in medicines for treatment of cancer, electroplating, photography, etc.

We wish to see the young students pursuing a career in engineering in different technical institutes and universities becoming aware of chemistry as an integral part and a dynamic process of the progress of technology. The study of solid state and its applications have given us ceramic floors to walk on and alloys to build our high-speed engines in bikes and cars. Further, polymer chemistry is product oriented, and of immeasurable importance to industry and economy today. The plastic cover of our cell phones, the dash board of our cars, the door laminates, the synthetic fibers in the dresses which we wear and even the artificial skin that doctors use for cosmetic surgery and prosthetics, are all possible due to extensive research in polymer chemistry.

The course would equip the students with the knowledge skill and make them adaptable to industry in the global context.

Each chapter in the book opens the gate to reputed research and development centres around the globe where Nobel laureates, engineers, chemists and metallurgists are working incessantly and diligently to make this world sustainable.

Objective

The primary focus of this textbook is to introduce the students to the concepts and application areas of chemistry in engineering. The chapters are structured in a style which would facilitate a comprehensive understanding of chemistry for the first year students. The language of the textbook is rendered to be student friendly as is the international practice today in the preparation of textbooks.

Each chapter begins with learning objectives and ends with key terms, objective-type and review questions and numerical problems along with answer key to further the understanding of the students and make them self-reliant.

Acknowledgments

We humbly and gratefully acknowledge all the great people who loved science and chemistry in the past, and those who love science today. It is due to their contributions that chemistry as a branch of knowledge has educated us, besides contributing to the well being of humanity. We are deeply grateful to scientists today who have dedicated their lives to futuristic investigations in valuable fields such as biochemistry, optimization, etc. This book gives us space and opportunity to remember and pay homage to people such as Jacobus Henricus van't Hoff for his work in chemical dynamics; Johann Friedrich Wilhelm Adolf von Baeyer for contributions to organic chemistry and the chemical industry, through investigations in organic dyes and aromatic compounds; Ernest Rutherford for his investigations into the disintegration of the elements and the chemistry of radioactive substances; Marie Curie for her discovery of the elements radium and polonium; Alfred Werner for his work on the linkage of atoms in molecules; Theodore William Richards for his accurate determinations of the atomic weight of a large number of chemical elements; Francis William Aston for discovery of isotopes by means of his mass spectrograph in a large number of non-radioactive elements, Carl Bosch for their contributions to the invention and development of chemical high pressure methods; William Francis Giauque for his contributions in the field of chemical thermodynamics, particularly concerning the behavior of substances at extremely low temperatures; Linus Carl Pauling for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances; Gerhard Ertl for his studies of chemical processes on solid surfaces and many more.

They belong to different countries but they make chemistry universal and humanistic. We acknowledge their works with gratitude and deep reverence.

We also acknowledge the encouragement and support of Prof. Manojranjan Nayak, Founder President of Siksha 'O' Anusandhan University and Prof. B.K. Sarap, Deputy Chairman, who are academicians with a vision. While preparing this text, Arushi and Gargi have filled our heart with their lilting smiles and divine innocence. We remain lovingly indebted to our parents whose blessings have always guided us. We acknowledge with gratitude the Wiley India team who worked more than us to make this text see the light of the day. We thank and bless Shivani, Wiley India, for her active coordination.

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1

Quantum Mechanical Approach to Atomic Structure

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Development of Quantum mechanics.
- Failure of classical mechanics.
- Explanation of the concept of quantization of energy from black body radiation.
- Explanation of particle and wave nature of light from photoelectric effect.
- Planck's quantum theory.
- Idea about dual nature of matter (de Broglie's relation).
- Atomic spectra.
- Heisenberg's uncertainty principle.
- Schrödinger wave equation.
- Eigen values and Eigen functions.
- Physical significance of ψ and ψ^2.

In 1809, John Dalton suggested that matter consists of large number of hard, dense and smallest possible particles called atoms. It means that atom is the ultimate particle of matter and is indivisible. However, various experiments proved that the atom consists of three major fundamental particles called electrons, protons and neutrons. Different atomic models have been developed to explain the structure of an atom. Bohr's atomic model is considered as the most important one. According to Bohr's atomic model, nucleus is situated at the center of atom and electrons move around it along a fixed circular path known as orbit. One of the major shortcomings of this model is that it treats electron as a particle only. However, de Broglie suggested that moving electron behaves as a particle as well as a wave. Considering the wave character of electron, Erwin Schrödinger, in 1926, derived a wave equation for electron in an atom. This is called wave mechanical model of atom, and led to the concept of atomic orbitals. According to this model, an electron keeps on moving in space towards or away from the nucleus, where the probability of finding electron is maximum. This space is called atomic orbital. Thus, an atomic orbital is defined as the space around the nucleus in which the probability of finding electron is very high.

1.1 Development of Quantum Mechanics

Quantum mechanics was developed to explain the inconsistencies found between the results of experiments conducted by scientists and predictions of classical mechanics. Some of such examples are cited as follows.

1. Classical mechanics predicts that any object is capable of radiating infinite amount of energy, when subjected to a temperature greater than absolute zero. This prediction was found wrong from the results of experiment on black body radiation.
2. The prediction of classical mechanics was again proven wrong, when scientists made it clear from the experiments that the atom is stable and consists of small positively charged nucleus surrounded by electron cloud.

These inconsistencies between classical mechanics and experimental observations provided the stimulus for the development of quantum mechanics.

Failure of Classical Mechanics

Any scientific theory is supported at least by one adequate experiment. If the experiment does not give any evidence in support of a theory, that theory becomes unacceptable and needs to be modified. In such a case, the concepts of the theory are called the failures or limitations of the theory.

Similarly, some concepts of classical mechanics went wrong with the results of experiments. These concepts were the reasons for the failure of classical mechanics. For example, classical mechanics considered energy as a continuous quantity, which was proved wrong by the experiment on black body radiation and atomic spectra. Experiments on photoelectric effect proved particle nature of light which was not considered by classical mechanics. According to classical mechanics, objects such as electrons, protons, neutrons, etc. possess only particle characteristics; whereas de Broglie suggested that any moving material object possesses both particle as well as wave nature. This was also experimentally verified. Thus, the important failures of classical mechanics are:

1. It could not explain the concept of quantization of energy (discontinuous or discrete nature of energy).
2. It could not explain dual character of light.
3. It could also not explain dual nature of matter or wave-particle duality.

1.2 Black Body Radiation

A **black body** is an object that is capable of emitting and absorbing radiations of all frequencies uniformly. In other words, an ideal black body does not radiate any amount of heat that is incident on it. This means it absorbs all the heat supplied to it and hence a black body is a good absorber of heat. Practically no such black body is known but a surface coated with lamp black is a very good approximation.

When a black body is heated to a high temperature, it emits radiations of all frequencies. So the black body is a good emitter. The radiation coming out from the black body is called **black body radiation**.

Assumptions of Classical Mechanics on Black Body Radiation

1. Figure 1 shows that the spectral density of a black body increases with increase in frequency at high temperature (6000 K). Spectral density is the energy, at frequency ν, per unit volume per unit frequency of the field of the black body at a temperature T. It can be given as:

$$\rho(\nu,T)\mathrm{d}\nu = \frac{8\pi kT\nu^2}{c^3}\mathrm{d}\nu \tag{1.1}$$

   where k is the Boltzmann constant, T is the temperature in absolute scale and c is the velocity of light. The spectral density is expressed as J/m^3/s.
2. It predicted that a black body will emit an infinite amount of energy at all temperatures above absolute zero. It means that energy is a continuous quantity.
3. Energy of radiation is directly proportional to square of the amplitude.

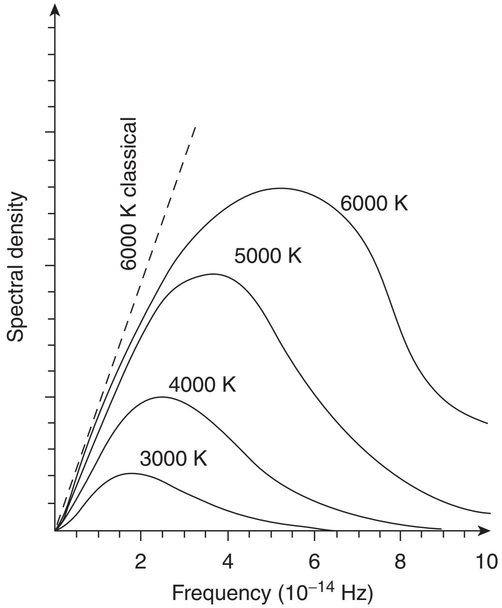


Figure 1 Dotted line shows the assumptions of classical mechanics for black body radiation at temperature 6000 K. Solid curves show the observations on black body radiation at different temperatures.

Observations from Experiments on Black Body Radiation

The assumptions of classical mechanics on black body radiation were found wrong based on the following observations.

1. Figure 1 shows that spectral density of the black body increases to a maximum and then decreases with increase in frequency.
2. It can also be observed from Figure 1 that at low temperatures low frequency radiations are possible and at high temperatures, high frequency radiations are possible. In other words, temperature of the black body is proportional to its frequency ($T \propto \nu$).
3. Again high energy corresponds to high temperature, which is consistent with our experience that if more power (at high temperature) is put into an electrical heater its color will change from red (low energy) to yellow (increasing energy). This means that energy of the radiation is proportional to temperature of the black body ($E \propto T$).

Considering these points, Max Planck realized that energy is proportional to frequency but not amplitude as considered by classical mechanics. He formulated that energy radiated by a black body is proportional to its frequency ($E \propto \nu$). Accordingly, he corrected the expression for spectral density of radiation of a black body as follows:

$$\rho(\nu,T)\mathrm{d}\nu = \frac{8\pi \mathrm{h}\nu^3}{c^3}\frac{1}{e^{\mathrm{h}\nu/kT}}\mathrm{d}\nu \tag{1.2}$$

where h is Planck’s constant.

Since frequency of radiation takes integral values and Planck's constant (h) has fixed value, hν takes a fixed or definite value. Hence, energy of radiation has a definite value and is quantized. Thus, black body radiation explained the concept of quantization of energy. Based on this, Max Planck put forward a theory which is known as **Planck's quantum theory**.

Planck's Quantum Theory

The postulates of Planck's quantum theory are as follows:

1. Energy is emitted or absorbed by a body discontinuously in the form of small packets.
2. Each small packet of energy is called quantum and each small packet of light energy is called photon.
3. The energy of a photon depends on the frequency of radiation. These two are related according to following relationship

$$E = \mathrm{h}\nu \tag{1.3}$$

where ν is the frequency radiation and h is Planck's constant.
Since $\nu = c/\lambda$, Eq. (1.3) can be written as:

$$E = \mathrm{h}\frac{c}{\lambda} \tag{1.4}$$

Problem 1

Electromagnetic radiation of the wavelength 242 nm is just sufficient to ionize Na atom. Calculate the ionization energy of sodium. Given that Avogadro number = 6.023×10^{23}, $c = 3 \times 10^8$ m/s and $h = 6.626 \times 10^{-34}$ Js.

Solution

Given that $\lambda = 242$ nm $= 242 \times 10^{-9}$ m.
We know that $E = (\mathrm{h}c)/\lambda$. Putting the values of h, c and λ, we get

$$E = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{242 \times 10^{-9}} = 8.21 \times 10^{-19}\ \mathrm{J}$$

For one atom $E_1 = 8.21 \times 10^{-19}$ J. Therefore, for one mole (Avogadro number) of atoms, $E_2 = 8.21 \times 10^{-19} \times 6.023 \times 10^{23}$ J/mol = 494.5 kJ/mol.
Thus, the ionization energy of sodium is 494.5 kJ/mol.

Problem 2

Energy of a photon is found to be 9.94×10^{-19} J. Calculate the wavelength associated with it.

Solution

We know that $$E = \mathrm{h}\nu = \frac{\mathrm{h}c}{\lambda}$$

Therefore, $$\lambda = \frac{\mathrm{h}c}{E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{9.94 \times 10^{-19}}$$

or $$\lambda = 1.999 \times 10^{-7} = 1.999 \times 10^{-7} \times 10^{9} = 199.9 \text{ nm}$$

Hence, the wavelength of the photon is 199.9 nm.

Concept Check

- Mention two significant causes for the failure of classical mechanics.
- What is quantization of energy?
- What is a black body?
- State Planck's quantum theory.

1.3 Photoelectric Effect

The phenomenon of ejection of electrons from a surface of a metal, when light of frequency greater than or equal to certain minimum frequency is made incident on it, is called photoelectric effect. This minimum frequency is called threshold frequency (ν_0).

When a photon of threshold frequency strikes a metal, it imparts its total energy (hν_0) to the metal surface. As a result, the electrons present on the metal surface are ejected. If the frequency of the light is less than ν_0, there will be no ejection of electrons. If the frequency (ν) of light striking the metal surface is higher than ν_0, the photon of this light will now impart more energy ($h\nu$) to the metal surface than that needed to eject the electrons. In such case, excess energy will be used to increase the kinetic energy (KE) or velocity of the ejected electrons. Thus, the ejected electron will move with kinetic energy which can be calculated as:

$$\mathrm{KE} = \frac{1}{2}mv^2 = \mathrm{h}\nu - \mathrm{h}\nu_0 = \mathrm{h}\nu - W_0 \tag{1.5}$$

where W_0 is called **work function**. It is the minimum amount of energy required to eject the electron from the metal surface.

Only a few metals show photoelectric effect under the action of visible light but many more show this effect under the action of more energetic ultraviolet light. The threshold frequency varies with nature of metals. For alkali metals such as, potassium (K), rubidium (Rb) and cesium (Cs), it is quite low and lies in visible region.

Assumptions of Classical Mechanics on Photoelectric Effect

1. Light is made incident as a plane wave over the whole metal surface. As a result, it is absorbed by many electrons present in the metal surface and these electrons are ejected. This statement predicted that light propagates only in form of waves.
2. Electrons are emitted from the metal surface by absorbing light of all frequencies, provided it must be sufficiently intense. It means that the ejection of electrons from the metal surface does not depend on the frequency of incident radiation.
3. The kinetic energy per electron increases with the intensity of incident light.

Observations from Experiments on Photoelectric Effect

1. It was observed that electrons are ejected from the metal surface by incident light of low intensities; and it was also observed that electrons are emitted from the metal surface, when light having frequency equal to or greater than certain minimum frequency known as threshold frequency (ν_0) is made incident on the metal surface.
2. Kinetic energy of the ejected electron depends on the frequency of incident light and is independent of light intensity. But the number of emitted electrons is proportional to the intensity of incident light.

Conclusion

1. Classical theory could not establish the relation between energy of light and its frequency (i.e., $E = \mathrm{h}\nu$).
2. Experiments on photoelectric effect revealed particle nature of light since electrons are emitted from metal surface when light having energy $\mathrm{h}\nu$ is made incident on it.
3. The phenomena like diffraction and interference provided evidence for wave nature of light.
4. Thus, it was concluded that light possesses particles which propagate in form of waves.

Problem 3

A photon of wavelength 4000 Å, strikes a metal surface. The work function of the metal being 2.13 eV, calculate the energy of incident photon in eV, the KE of the emitted electron and the velocity of the electron.

Solution

Energy of incident photon, $E = \mathrm{h}\nu$

or

$$E = \mathrm{h}\frac{c}{\lambda} = \frac{6.626\times10^{-34}\times3\times10^{8}}{4000\times10^{-10}} = 4.969 \times 10^{-19}\ \mathrm{J}$$

Since 1 J = 1/ 1.602 × 10^{-19} eV, the above expression can be written as:

$$E = \frac{4.969\times10^{-19}}{1.602\times10^{-19}}\ \mathrm{eV} = 3.10\ \mathrm{eV}$$

We know that

$$\mathrm{KE} = \frac{1}{2}mv^2 = \mathrm{h}\nu - W_0$$

where W_0 = work function = 2.13 eV and m = mass of electron = 9.1 × 10^{-31} kg.
So, KE = 3.10 − 2.13 = 0.97 eV.

Also, KE = $\frac{1}{2}mv^2$, so

$$\frac{1}{2}mv^2 = 0.97 \times 1.602 \times 10^{-19}\ \mathrm{J}$$

(Since 1 eV = 1.602×10^{-19} J)

$$v = \sqrt{\frac{2 \times 0.97 \times 1.602 \times 10^{-19}}{9.1 \times 10^{-31}}} = 5.85 \times 10^{5}\,\text{m/s}$$

Problem 4

Calculate the work function of a metal surface if the velocity of the ejected electron is 6.46×10^{5} m/s, when irradiated by a light of 200 nm.

Solution

We know that

$$\text{KE} = \text{h}\nu - W_0 \Rightarrow W_0 = \text{h}\nu - \text{KE}$$

where W_0 = work function of a metal.

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{2} \times 9.1 \times 10^{-31} \times (6.46 \times 10^{5})^2 = 189.87 \times 10^{-21}\ \text{J}$$

where m = mass of ejected electron = 9.1×10^{-31} kg.
Wavelength of incident light (λ) = 200 nm = 200×10^{-9} m. Therefore,

$$\text{h}\nu = \frac{\text{h}c}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{200 \times 10^{-9}} = 9.939 \times 10^{-19}\ \text{J}$$

Substituting in expression for work function, we get

$$W_0 = 9.939 \times 10^{-19} - 189.87 \times 10^{-21} = 8.049 \times 10^{-19}\ \text{J}$$

$$= \frac{8.049 \times 10^{-19}}{1.602 \times 10^{-19}} = 5.024\ \text{eV}$$

Concept Check

- What is photoelectric effect?
- The work function for metallic cesium is 2.14 eV. Calculate the KE and speed of the electrons ejected by light of wavelength 250 nm.
- A light of wavelength 150 nm strikes platinum surface having a work function 5 eV. Calculate the velocity of ejected electron.

1.4 Wave and Particle Characteristics of Matter (de Broglie's Relation)

According to Einstein theory,

$$E = mc^2 \tag{1.6}$$

According to Max Planck theory,

$$E = \mathrm{h}\nu \tag{1.7}$$

de Broglie considered the Eqs. (1.6) and (1.7) and derived that

$$mc^2 = \mathrm{h}\nu = \frac{\mathrm{h}c}{\lambda}$$

or

$$\lambda = \frac{\mathrm{h}}{mc} \tag{1.8}$$

where m is the mass of light particle, c is the velocity of light, λ is the wavelength and h is Planck's constant.

Equation (1.8) shows that light particle having mass m moves with velocity c is associated with a wave of wavelength λ. de Broglie suggested that any material object having mass m and moving with velocity v can be associated with a wave of a definite wavelength as moving light particles possess. Hence, he derived the relation

$$\lambda = \frac{\mathrm{h}}{mv} \tag{1.9}$$

where m is mass of an object, v is velocity of the object, λ is wavelength of the object, h is Planck's constant.

Equation (1.9) is called **de Broglie's relation**, which shows that any material object moving with certain velocity possesses particle as well as wave character.

Experimental Verification of de Broglie's Relation

Different experiments were conducted to verify de Broglie's relation. Some of them are discussed as follows.

The important experiment carried out by Davisson and Germer proved that particles like electrons possess wave-like character. In this experiment, electrons were emitted from a hot filament and accelerated by a potential ranging between 40 and 68 V before striking a nickel plate (Figure 2).

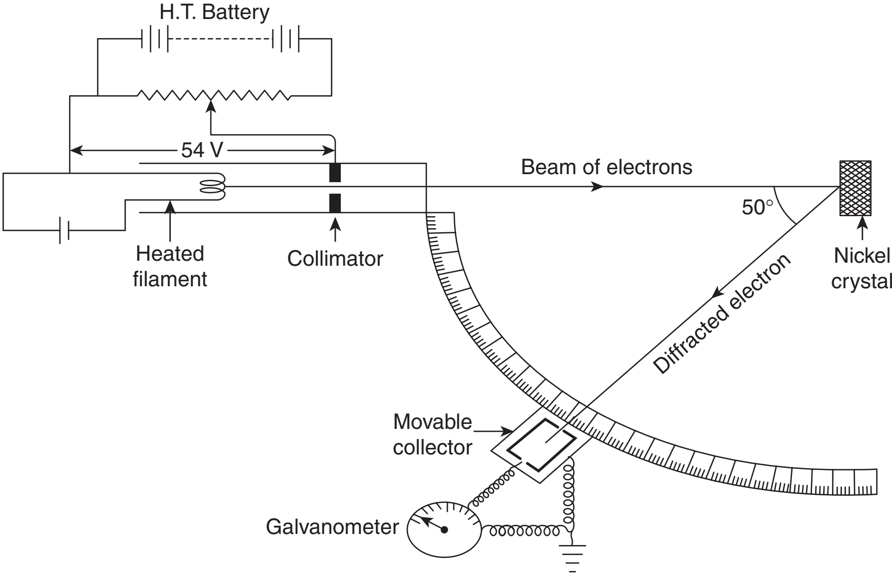


Figure 2 Davisson and Germer experiment for verification of de Broglie's equation.

They found that the impact of electrons resulted in the production of diffraction patterns which were similar to those given by X-rays under similar conditions. Since X-rays possess wave character, the experiment gave direct evidence for wave character of electrons.

Let an electron be accelerated by a potential V_0. Then its kinetic energy will be

$$\mathrm{KE} = \frac{1}{2}mv^2 = eV_0 \tag{1.10}$$

or

$$v = \sqrt{\frac{2eV_0}{m}} \tag{1.11}$$

or

$$v = \sqrt{\frac{2\mathrm{KE}}{m}} \tag{1.12}$$

where, m is the mass of electron, v is the velocity of electron and e is the charge of electron.

If the electron possesses wave character, it must be associated with a wave and its wavelength can be given by de Broglie's relation as

$$\lambda = \frac{\mathrm{h}}{mv} = \frac{\mathrm{h}}{m\sqrt{\dfrac{2eV_0}{m}}}$$

or

$$\lambda = \frac{\mathrm{h}}{\sqrt{2meV_0}} \tag{1.13}$$

or

$$\lambda = \frac{\mathrm{h}}{\sqrt{2m\mathrm{KE}}} \tag{1.14}$$

Equations (1.13) and (1.14) are different forms of de Broglie's equation.

Putting the values of h, m and e in Eq. (1.13), we get

$$\lambda = \frac{6.626\times10^{-34}}{(2\times9.1\times10^{-31}\times1.6\times10^{-19})V_0^{1/2}}$$

or

$$\lambda = 12.26\times10^{-10}\,V_0^{-1/2} \tag{1.15}$$

If potentials are varied between 10 and 10000 V, λ should vary between 3.877 Å and 0.1266 Å. It is well known that X-rays have wavelengths of this order. Hence, moving electrons possess wave-like character.

Limitation of de Broglie's Relation

From de Broglie's equation, it is known that wavelength of a moving object is inversely proportional to the product of its mass and its velocity ($\lambda \propto 1/mv$). It means that the wavelength of a microscopic object would be longer if its mass is small. On the other hand, it would be shorter for a macroscopic object as its mass is large. For a very big object, the wavelength would be too small to be measured. Thus, de Broglie's concept loses its importance when applied to macroscopic objects. Hence, it is significant only for microscopic particles.

Problem 5

Calculate the wavelength of de Broglie wave associated with an electron accelerated by a voltage of 50 kV.

Solution

Given that V_0 = 50 kV = 50000 V, charge of electron (e) = 1.6×10^{-19} C, mass of electron (m) = 9.1×10^{-31} kg.

Wavelength of the electron is given by

$$\lambda = \frac{\mathrm{h}}{\sqrt{2meV_0}}$$

or

$$\lambda = \frac{6.626 \times 10^{-34}}{\sqrt{2(9.1 \times 10^{-31})(1.6 \times 10^{-19})(50000)}}$$

$$= 0.549 \times 10^{-11}\ \mathrm{m}$$

Problem 6

The kinetic energy of a subatomic particle is 5.65×10^{-25} J. Calculate the frequency of particle wave.

Solution

We know that

$$\mathrm{KE} = \frac{1}{2} mv^2$$

or

$$v = \sqrt{\frac{2\mathrm{KE}}{m}}$$

Now,

$$\lambda = \frac{\mathrm{h}}{mv} = \frac{\mathrm{h}}{m\sqrt{\dfrac{2\mathrm{KE}}{m}}} = \frac{\mathrm{h}}{\sqrt{2m\mathrm{KE}}}$$

Again,

$$\nu = \frac{v}{\lambda} = \frac{\sqrt{2\mathrm{KE}/m}}{\mathrm{h}/\sqrt{2m\mathrm{KE}}}$$

or

$$\nu = \frac{2\mathrm{KE}}{\mathrm{h}} = \frac{2 \times 5.65 \times 10^{-25}}{6.62 \times 10^{-34}} = 1.7 \times 10^{9}\ \mathrm{s}^{-1}$$

Concept Check

- Write de Broglie's equation and explain the terms involved in it.
- Two particles A and B are in motion. If the wavelength associated with particle A is 0.1 Å, calculate the wavelength of particle B, if its momentum is twice that of A.
- An electron moves in an electric field with KE of 2.5 eV. What is its associated de Broglie wavelength?
- Calculate the de Broglie wavelength of a body of mass 1 mg moving with a velocity of 10 m/s.

1.5 Atomic Spectra

When an electric discharge is passed through H_2 gas taken in a discharge tube under low pressure and the emitted radiation is analyzed with the help of a spectrograph, it is found to consist of a series of sharp lines. This series of lines is known as line or atomic spectrum of hydrogen. The different series of lines are Lyman, Balmer, Paschen, Brackett and Pfund series. These lines are discontinuous. So atomic spectra explained that energy in the form of radiation is discontinuous or energy is quantized. Wave number $(\bar{\nu})$ for different lines in H spectra is calculated as follows:

$$\bar{\nu} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \tag{1.16}$$

where R_H is Rydberg constant, n_1 is the lower energy level in H atom, n_2 is the higher energy level in H atom The Rydberg constant is given by

$$R_H = \frac{2\pi m Z^2 e^4 k^2}{c\mathrm{h}} = 1.097 \times 10^7 \mathrm{m}^{-1} \quad \text{(for hydrogen)}$$

where m is mass of electron, Z is atomic number, e is charge on electron, c is velocity of light and h is Planck's constant.

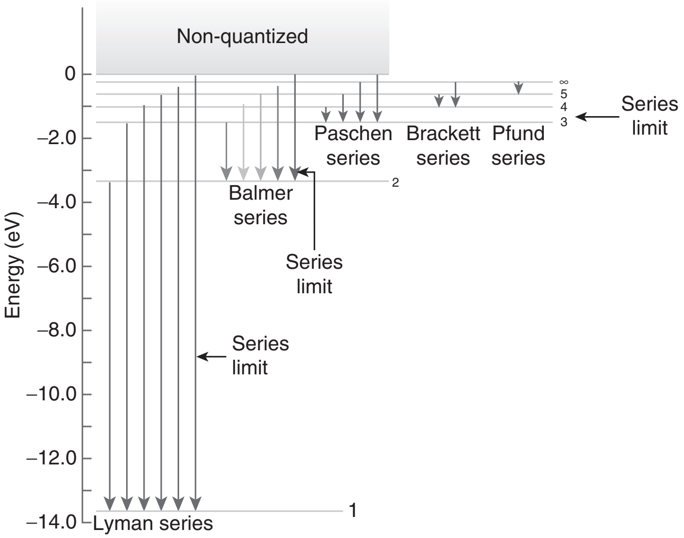


Figure 3 Spectral series in hydrogen spectrum.

The characteristics of series of lines in hydrogen spectrum are given as follows:

1. **Lyman series:** It corresponds to ultraviolet region of electromagnetic spectrum. This series is formed when electrons from higher energy levels ($n_2 = 2, 3, 4 \ldots$) jump to first energy level ($n_1 = 1$) in the hydrogen atom.
2. **Balmer series:** It corresponds to visible region of electromagnetic spectrum. When electrons jump from higher energy levels ($n_2 = 3, 4, 5\ldots$) to second energy level ($n_1 = 2$) in the hydrogen atom, this series is formed.
3. **Paschen series:** This series falls in infrared region of electromagnetic spectrum. It is formed by the transition of electrons from higher energy levels ($n_2 = 4, 5, 6\ldots$) to third energy level ($n_1 = 3$) in the hydrogen atom.
4. **Brackett series:** It also corresponds to infrared region of electromagnetic spectrum. When electrons jump from higher energy levels ($n_2 = 5, 6, 7\ldots$) to fourth energy level ($n_1 = 4$) in the hydrogen atom, this series is formed.
5. **Pfund series:** This series falls in infrared region of electromagnetic spectrum. It is formed by the transition of electrons from higher energy levels ($n_2 = 6, 7, 8,\ldots$) to fifth energy level ($n_1 = 5$) in the hydrogen atom.

The series of lines observed in different regions of the spectrum have been shown in Table 1 and Figure 3.

Table 1 Spectral Series Found in Atomic Hydrogen

Series	*Lyman*	*Balmer*	*Paschen*	*Brackett*	*Pfund*
Region of Spectrum	Ultraviolet	Visible/ ultraviolet	Infrared	Infrared	Infrared
Equation	$\bar{v} = R_{\mathrm{H}}\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$ where $n = 2, 3, \ldots$	$\bar{v} = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ where $n = 3, 4, \ldots$	$\bar{v} = R_{\mathrm{H}}\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$ where $n = 4, 5, \ldots$	$\bar{v} = R_{\mathrm{H}}\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$ where $n = 5, 6, \ldots$	$\bar{v} = R_{\mathrm{H}}\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$ where $n = 6, 7, \ldots$

Problem 7

Calculate the energy emitted when electrons of 1 g atom of hydrogen undergo transition giving the spectral line of the lowest energy in the visible region of its atomic spectrum. Given that $R_H = 1.1 \times 10^7\ m^{-1}$, $c = 3 \times 10^8\ m/s$, $h = 6.62 \times 10^{-34}\ Js$.

Solution

Spectral line in the visible region of the hydrogen spectra is obtained when electrons jump from higher energy level to second energy level ($n_1 = 2$). Again the lowest energy in the visible region is obtained when electrons in the hydrogen atom jump from third energy level ($n_2 = 3$) to second energy level.

We know that,

$$\bar{\nu} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or $$\frac{1}{\lambda} = 1.1\times10^7\left[\frac{1}{4} - \frac{1}{9}\right] = 1.1\times10^7\left[\frac{9-4}{36}\right] = 1.1\times10^7\left[\frac{5}{36}\right]$$

or $$\lambda = \frac{36}{1.1\times10^7\times5} = 6.55\times10^{-7}\text{ m}$$

Energy emitted from one atom of hydrogen,

$$E = \text{h}\frac{c}{\lambda} = \frac{6.626\times10^{-34}\times3\times10^8}{6.55\times10^7} = 3.03\times10^{-19}\text{ J}$$

Energy emitted from 1g atom of hydrogen = $3.03 \times 10^{-19} \times 6.023 \times 10^{23} = 182.5$ kJ

Problem 8

Calculate the wave number and frequency of the spectral line involving the transition of electron from n =1 to n = 2 in a hydrogen atom. Given, Rydberg constant = $1.0974 \times 10^7 m^{-1}$.

Solution

Given that $n_1 = 1$, $n_2 = 2$ and $R_H = 1.0974 \times 10^7\text{m}^{-1}$.

$$\bar{\nu} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad (\text{where } \bar{\nu} = \text{wave number})$$

or $$\bar{\nu} = 1.0974\times10^7\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = 1.0974\times10^7\left[\frac{1}{1} - \frac{1}{4}\right] = 1.0974\times10^7\left[\frac{3}{4}\right] = 0.822\times10^7\text{ m}^{-1}$$

or $$\frac{1}{\lambda} = 0.822\times10^7\text{ m}^{-1}$$

or $$\nu = 3\times10^8\text{ ms}^{-1}\times0.822\times10^7\text{ m}^{-1} \quad (\text{as } \nu = \frac{c}{\lambda})$$

$$= 2.466\times10^{15}\text{ s}^{-1}$$

Concept Check

- Which series of lines in hydrogen spectra corresponds to visible region of electromagnetic spectra?
- Calculate the wavelength corresponding to the spectral lines. $n_1 = 2$ and $n_2 = 3$. (Value of Rydberg constant = $1.097 \times 10^7\text{m}^{-1}$)
- Name the different series of lines that appear in hydrogen spectra.

1.6 Heisenberg's Uncertainty Principle

We can determine both position and momentum (or velocity) of a macroscopic object instantly. Consequently, the path of such an object can be predicted accurately. However, the position and momentum of microscopic particles like electrons cannot be determined accurately. In 1927, Werner Heisenberg put forward this fact in the form of uncertainty principle which states that:

It is impossible to determine both position and momentum (or velocity) of microscopic particles simultaneously with great accuracy.

Mathematical Expression

$$\Delta x \times \Delta p \geq \frac{\mathrm{h}}{4\pi} \tag{1.17}$$

where Δx is uncertainty in position and Δp is uncertainty in momentum. Substituting for $\Delta p = m\Delta v$, we get

$$\Delta x \times m \times \Delta v \geq \frac{\mathrm{h}}{4\pi}$$

$$\Delta x \times \Delta v \geq \frac{\mathrm{h}}{4\pi m} \tag{1.18}$$

where Δv is uncertainty in velocity and m is mass of the microscopic particle.

Explanation

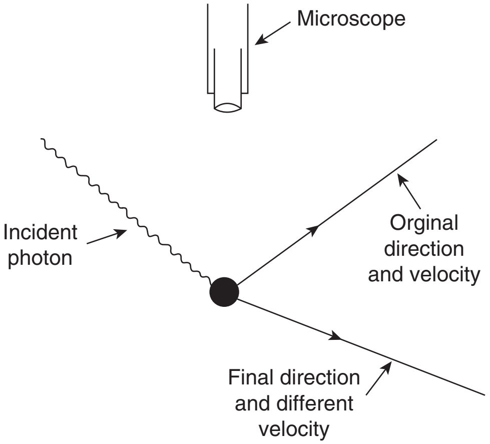


Figure 4 Change in the direction and velocity of an electron by the impact of a photon of light.

Let us consider an electron moving in its orbit around the nucleus in an atom (Figure 4). In order to locate it, a photon of high energy is made incident as it is a small object. As a result, the electron absorbs some amount of energy from the incident photon and will move with greater velocity. Hence, the velocity of the moving electron cannot be determined exactly, when its position is determined.

In order to determine the velocity of the electron, it is required to use a photon of less energy, which will not increase its velocity. On the other hand, the electron cannot be traced by using a photon of less energy since it is a small particle. Hence, the position of the electron cannot be determined, if its velocity is determined.

Problem 9

Calculate the uncertainty in the velocity of a bullet weighing 10 g whose position is known with ± 0.01mm accuracy.

Solution

Given that $m = 10\text{ g} = 10 \times 10^{-3}$ kg and $\Delta x = \pm\, 0.01\text{mm} = 0.01 \times 10^{-3}$ m.
According to Heisenberg's uncertainty principle,

$$\Delta x \times \Delta v = \frac{\mathrm{h}}{4\pi m}$$

$$\Delta v = \frac{\mathrm{h}}{4\pi m \Delta x} = \frac{6.626\times10^{-34}}{4\times3.14\times10\times10^{-3}\times0.01\times10^{-3}} = 0.527\times10^{-27}\text{ m/s}$$

Thus, uncertainty in velocity of the bullet is 0.527×10^{-27} m/s.

Problem 10

On the basis of the uncertainty principle explain why electrons cannot exist within the nuclei of the atoms.

Solution

The radius of the nucleus = 10^{-14} m. If electrons were to exist within the nucleus, then the uncertainty in its position (Δx) is equal to the radius of the nucleus. So $\Delta x = 10^{-14}$. Using mass of electron = 9.1×10^{-31} kg and Heisenberg's uncertainty principle, we have

$$\Delta v \geq \frac{\mathrm{h}}{4\pi m \Delta x}$$

or

$$\Delta v \geq \frac{6.626\times10^{-34}}{4\times3.14\times9.1\times10^{-31}\times10^{-14}} = 6\times10^{8}\text{ m/s}$$

Since the uncertainty in velocity is much larger than the velocity of light, the electron cannot exist within the nucleus.

Concept Check

- A vehicle weighing 800 kg is moving with a speed accuracy of 3.6 km/h and positional accuracy of 16 m. Is the uncertainty principle valid? Explain.

- What is the order of uncertainty in momentum if the uncertainty in position of a particle is 10^{-34}?
- Explain why the effect of Heisenberg uncertainty principle is only significant in case of microscopic particles and not in macroscopic objects.

1.7 Schrödinger Wave Equation

Moving electrons behave both as particles and as waves. If the electrons behave as a wave, there must be a wave equation to describe their behavior. In 1926, Erwin Schrödinger, gave a wave equation to describe the wave behavior of electrons in atoms and molecules. In Schrödinger wave model of atom, the discrete energy levels or orbits proposed by Bohr are replaced by mathematical function ψ. Therefore, ψ may be regarded as the wave mechanical equivalent of the electron orbit in classical theory. Due to this the electron wave function is frequently referred to an orbital or an orbital wave function.

The Schrödinger wave equation for an electron wave propagating in three dimensions in space, is written as follows:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0 \tag{1.19}$$

or

$$\nabla^2\psi+\frac{8\pi^2 m}{\mathrm{h}^2}(E-V)\psi=0 \tag{1.20}$$

where $\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$

and ∇ is known as Laplacian operator, *m* is the mass of electron (particle), *E* is the total energy of the particle and *V* is the potential energy. Equation (1.20) can be written as

$$\nabla^2\psi+\frac{8\pi^2 m}{\mathrm{h}^2}E\psi-\frac{8\pi^2 m}{\mathrm{h}^2}V\psi=0$$

or

$$\nabla^2\psi-\frac{8\pi^2 m}{\mathrm{h}^2}V\psi=-\frac{8\pi^2 m}{\mathrm{h}^2}E\psi$$

or

$$-\nabla^2\psi+\frac{8\pi^2 m}{\mathrm{h}^2}V\psi=+\frac{8\pi^2 m}{\mathrm{h}^2}E\psi \tag{1.21}$$

Multiplying $\mathrm{h}^2/8\pi^2 m$, in both the sides of Eq. (1.21), we get,

$$\left[-\frac{\mathrm{h}^2}{8\pi^2 m}\nabla^2+V\right]\psi=E\psi \tag{1.22}$$

If $\hbar=\mathrm{h}/2\pi$, Eq. (1.22) becomes

$$\left(-\frac{\hbar^2}{2m}\nabla^2+\mathrm{V}\right)\psi=E\psi$$

$$\hat{\mathrm{H}}\psi = E\psi \tag{1.23}$$

Equation (1.23) is simplest form of Schrödinger wave equation where $\hat{\mathrm{H}}$ is called the Hamiltonian operator and

$$\hat{\mathrm{H}} = -\frac{\hbar^2}{2m}\nabla^2 + V$$

Hence, Hamiltonian operator ($\hat{\mathrm{H}}$) consists of two parts. One is kinetic energy (KE) part $\left(-\frac{\hbar^2}{2m}\nabla^2\right)$ and the other one is electrostatic potential energy (PE) part (V).

Schrödinger Wave Equation for H Atom

Let the charge on a proton is $+e$ and that on an electron is $-e$. In H atom, there is one proton in the nucleus and one electron in the extra nuclear part. So the nuclear charge in the H atom is $+e$. Let the distance between nucleus and electron in the H atom be r. Then the potential energy can be given by:

$$V = -\frac{e^2}{r} \tag{1.24}$$

Putting the value of V from Eq. (1.24) in Eq. (1.19), we get

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{\mathrm{h}^2}\left[E - \left(\frac{-e^2}{r}\right)\right]\psi = 0$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{\mathrm{h}^2}\left[E + \frac{e^2}{r}\right]\psi = 0 \tag{1.25}$$

Equation (1.25) represents Schrödinger wave equation for H atom.

Eigen Values and Eigen Functions

The Schrödinger wave equation is a differential equation of second order and will have many solutions when it is solved. Many of them are imaginary and have no significance. Those solutions are significant which give certain definite and acceptable values of the total energy E. The acceptable values of the total energy E given by a solution is called **Eigen value** and the corresponding wave function ψ is called **Eigen function**.

Conditions of an Eigen Function or an Acceptable Wave Function

1. It must be **single valued** because the probability of finding the electron at any point in space has one and only one value.
2. It must be **finite**. This is due to the fact that an infinite value assigned to ψ at any point would make ψ^2 infinite, which means that the electron is fixed exactly at that point and that is never the case.
3. Since the total probability of finding an electron somewhere in space must be unity, the wave function is **normalized**. So ψ should satisfy the following equation:

$$\int_{-\infty}^{+\infty} \psi^2 \mathrm{d}\tau = 1$$

4. It should be **continuous**.

Interpretation of Wave Function

According to Heisenberg's uncertainty principle, the exact position of electron moving around the nucleus with a particular velocity cannot be determined. So we have to use probability in order to locate the electron in a given region. In other words, we use a probability function for the location of electron. Let this function be $\rho(x, y, z)$. Then the probability of finding an electron in a small cubic volume of dimensions dx, dy, dz can be given by $\rho(x, y, z) \cdot \mathrm{d}x\mathrm{d}y\mathrm{d}z$. The volume of this small cube is dxdydz or dτ. The function is also known as **probability density**.

Let us consider that the whole space is divided into a number of such volume elements. The total probability of finding the electron in the whole space will be given by the summation of all the terms like $\rho\,\mathrm{d}x\mathrm{d}y\mathrm{d}z$ or $\rho\mathrm{d}\tau$ (Figure 5). It can be given by

$$\int_{-\infty}^{+\infty} \rho \mathrm{d}x\mathrm{d}y\mathrm{d}z \quad \text{or} \quad \int_{-\infty}^{+\infty} \rho \mathrm{d}\tau$$

Since the electron is somewhere in the space, the total probability of finding electron must be equal to unity. Thus,

$$\int_{-\infty}^{+\infty} \rho \mathrm{d}x\mathrm{d}y\mathrm{d}z = 1 \tag{1.26}$$

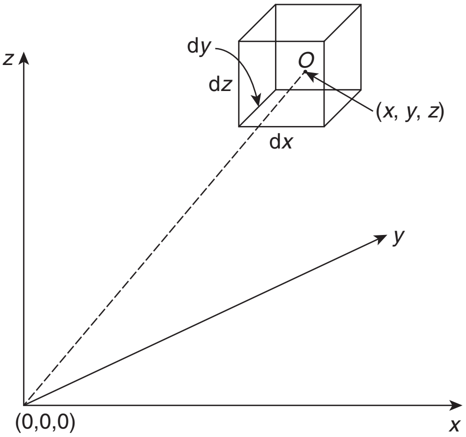


Figure 5 Representation of small volume element dxdydz surrounding the point O (x, y, z).

Let us consider a wave function $\psi(x, y, z)$ for the electron. In such case ψ represents the amplitude of electron wave. The intensity of the wave is measured by the square of its amplitude [i.e., $\psi^2(x, y, z)$]. Again the intensity depends on the probability of finding the electron in a given region in space which is given by $\rho(x, y, z)$. Thus,

$$\rho(x, y, z) \propto \psi^2(x, y, z)$$

$$\rho(x, y, z) = k\,\psi^2(x, y, z) \tag{1.27}$$

where k is a constant of proportionality.

If $\psi(x, y, z)$ is the solution of Schrödinger equation, then ψ multiplied by any constant, will also be the solution of the same wave equation. This means, we can take $(1/\sqrt{k})\psi$ instead of ψ in Eq. (1.27). So,

$$\rho(x, y, z) = k\frac{1}{k}\psi^2(x, y, z)$$

or

$$\rho(x, y, z) = \psi^2(x, y, z) \tag{1.28}$$

Putting the value of $\rho(x, y, z)$ from Eq. (1.28) in Eq. (1.26), we get,

$$\int_{-\infty}^{+\infty} \psi^2 \mathrm{d}\tau = 1 \tag{1.29}$$

Thus, ψ^2 represents probability density or probability of finding electron around the nucleus.

Key Terms

Classical mechanics
Quantum mechanics
Quantization of energy
Dual nature of matter
Black body radiation
Photoelectric effect
Dual nature of light
Threshold frequency
de Broglie's concept
Hydrogen spectra
Rydberg constant
Heisenberg uncertainty principle
Schrödinger wave equation
Atomic orbital
Eigen values and Eigen functions
Wave function

Objective-Type Questions

Multiple-Choice Questions

1. The wave mechanical model of atom is based on
   - **a.** de Broglie concept of dual nature of matter.
   - **b.** Heisenberg's uncertainty principle.
   - **c.** Schrödinger wave equation.
   - **d.** All of the above.
2. The energy of n^{th} Bohr orbit of hydrogen atom is given by the relation.

   $$E_n = \frac{2.18 \times 10^{-18}}{n^2} \text{J}$$

   The frequency of the light emitted when an election jumps from third to the first orbit is ($h = 6.6 \times 10^{-34}$ Js)
   - **a.** 1.65×10^{15} s^{-1}
   - **b.** 1.65×10^{16} s^{-1}
   - **c.** 1.65×10^{17} s^{-1}
   - **d.** 1.65×10^{18} s^{-1}
3. In an electron microscope, electrons are accelerated to great velocities. Calculate the wavelength of an electron traveling with a velocity of 7.0 megameters per second. The mass of electron is 9.1×10^{-28} g.
   - **a.** 1.0×10^{-13} m
   - **b.** 1.0×10^{-7} m
   - **c.** 1.0 m
   - **d.** 1.0×10^{-10} m
4. Heisenberg's uncertainty principle precludes the exact simultaneous measurement of
   - **a.** charge density and probability.
   - **b.** position and momentum.

c. position and direction.
d. velocity and energy.

5. Which of the following condition is incorrect for well-behaved wave function ψ?
   a. ψ must be finite.
   b. ψ must be single valued at any particular point.
   c. ψ must be positive.
   d. ψ must be continuous function of its coordinates.

Fill in the Blanks

1. In the photoelectric effect, the kinetic energy of ejected electrons ______ with increase in wavelength of radiation.
2. _______ gives the probability of finding an electron around the nucleus.
3. An electron can move only in that orbit in which angular momentum of the electron is integral multiple of ______.
4. The wave character of an electron was experimentally verified by ________.
5. The correct Schrödinger wave equation for an electron, in a potential field V, in three dimensions is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\underline{\qquad}(E-V)\psi=0$$

Review Questions

Short-Answer Questions

1. If the wave number of electromagnetic radiation is $\bar{\nu}$, what will be its energy?
2. What is meant by quantization of energy?
3. Write the Einstein's photoelectric equation and define each term involved therein.
4. What is spectral density?
5. What do you understand by dual character of matter?
6. What is the physical significance of ψ^2?
7. Write the Schrödinger's equation and define each term involved in the equation.
8. What are the necessary conditions a wave function must satisfy?
9. What is the physical significance of ψ?
10. What is threshold frequency?
11. What are Eigen values and Eigen functions?
12. Write the limitations of de Broglie equation.
13. Why can de Broglie equation not be applicable for macroscopic objects?
14. What do you mean by black body radiation?
15. How are matter waves different from electromagnetic waves?

Long-Answer Questions

1. What is photoelectric effect? How did it help in explaining failure of classical mechanics?
2. How could black body radiation explain the concept of quantization of energy?

3. How de Broglie equation was experimentally verified? Explain with example.
4. Derive de Broglie equation for matter wave.
5. State and explain Heisenberg's uncertainty principle.

Numerical Problems

1. The energy of a photon is 20 eV. Find the momentum and wavelength of the photon.
2. A cricket ball weighing 100 g is to be located within 0.1 Å. What is the uncertainty in its velocity?
3. Calculate the de Broglie's wavelength for an electron moving with a velocity equal to one hundredth that of light.
4. If the wavelength of an electron is 0.5 nm, what is the velocity of the electron?
5. If an electron falls through a potential difference of 1 V, it acquires an energy of 1 eV and if the electron is to have a wavelength of 0.1 nm, what is the potential difference?
6. Calculate the velocity of an ejected electron, when a light of wavelength 500 nm strikes a metal surface with a work function of 1.5 eV.
7. What is the equivalent of energy unit 10 cm^{-1} in Joules per photon?
8. An electron is accelerated to one tenth the velocity of light. Suppose its velocity can be measured with a precision of ± 1%, what will be its uncertainty in position.

Answers

Multiple-Choice Questions

1. (d)
2. (a)
3. (d)
4. (b)
5. (c)

Fill in the Blanks

1. decreases
2. ψ^2
3. $\dfrac{h}{2\pi}$
4. Germer
5. $\dfrac{8\pi^2 m}{h^2}$

Numerical Problems

1. Momentum = 10.68×10^{-27} kg m/s; wavelength = 0.62×10^{-7} m
2. 0.527×10^{-22} m/s
3. 0.242×10^{-9} m
4. 1.456×10^{-22} m/s
5. 6.628×10^{-3} V
6. 0.5884×10^{6} m/s
7. 1.987×10^{-22} J
8. $\geq 1.93 \times 10^{-10}$ m

2 Chemical Bonding

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Valence bond theory of chemical bonding and its limitations.
- Hybridization and shapes of some molecules.
- Molecular orbital theory and its application to explain formation of homonuclear and heteronuclear diatomic molecules.
- Nature of metallic bond.

A chemical bond, which apparently exists between atoms in a molecule, is a *force* that holds bonded atoms together. Basically, it is the same kind of electrostatic attraction that binds the electrons of an atom to its positively charged nucleus. Chemical bonding occurs between two atoms when their electrons are simultaneously attracted by two nuclei and it causes the energy of the combining atoms to become lower than when they are apart.

There is no single satisfactory theory which would explain the concept of bonding in all types of compounds and also predict their structures, energies and properties. Initially, the concept of a chemical bond was explained by a few classical models which assumed that electrons and ions behave as point charges that attract and repel according to the laws of classical mechanics and electrostatics. However, these models apply only to certain classes of compounds and explain only a restricted range of phenomena. Since the development of quantum theory in 1920s, the chemical bond has been explained by quantum mechanical models. We shall look into the different models proposed.

The first ever theory to explain the formation of chemical bond was proposed by Kossel and Lewis and is known as the electronic theory of valency. The theory was based on the following observations:

1. The electrons in the outermost shell/orbit of an atom are called valence shell electrons. These are responsible for most of the properties of the elements.
2. Elements which have two or eight electrons in the outermost shell, that is, have their octet complete are stable and do not combine chemically either with each other or other elements.

According to the theory, the formation of a chemical bond between two or more atoms can be explained as tendency of elements to attain stable configuration of electrons in the outermost shell. The combining atoms may rearrange their electrons either by complete transfer of electrons from one atom to another or by sharing of electrons.

2.1 Valence Bond Theory

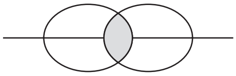
Valence bond theory is one of the basic theories, along with molecular orbital theory, developed to explain chemical bonding based on quantum mechanics. According to valence bond theory, a covalent bond is formed between two atoms in a molecule, when the half-filled valence atomic orbitals (AOs) of the two atoms containing unpaired electron overlap with one another and the electrons pair up in the overlap region. Due to the overlapping, electrons are localized between the atoms in the bond region. When the attractive forces (electron–nucleus of two different atoms) are stronger than the repulsive forces (electron–electron or nucleus–nucleus), energy is released; lowering of energy makes the molecule stable. This theory proposes that maximum overlap leads to the formation of the strongest possible bonds.

The postulates of the valence bond theory of covalent bonding are as follows:

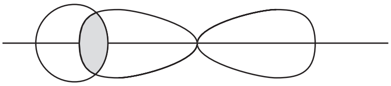
1. A covalent bond is formed due to the overlap of the outermost half-filled atomic orbitals of the combining atoms. The extent of overlap determines the strength of this bond.
2. The two half-filled orbitals involved in the bond formation should contain electrons of opposite spins.
3. Completely filled orbitals do not take part in the bond formation.
4. The non-spherical orbitals such as *p* and *d* orbitals tend to form bonds in the direction of maximum overlap.
5. When two orbitals are of same energy, the orbital which is non-spherical (*p* or *d* orbital) forms stronger bonds than the spherically symmetrical orbital (*s* orbital).

This overlap of orbitals leads to the formation of two types of covalent bonds, namely, sigma (σ) and *pi* (π):

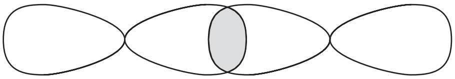
1. Sigma (σ) bonds are formed when the orbitals of two shared electrons overlap head-to-head. The overlapping AOs can be of different types, for example, a σ bond may be formed by the *s*–*s*, *s*–*p*, *s*–*d*, *p*–*p*, *p*–*d* or *d*–*d* overlapping of AOs. Some of the possible overlaps leading to a σ bond are:
   - *s*–*s* orbital overlap:

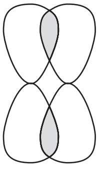
   - *s*–*p* orbital overlap:

   - *p*–*p* orbital overlap:

   For example in the case of H_2 molecule, H—H σ bond is formed by the *s*–*s* orbital overlap of the two hydrogen atoms containing one unpaired electron each; while in an F_2 molecule, the F—F bond is formed by the overlap of p_x orbitals of the two F atoms containing an unpaired electron each. Since the nature of the overlapping orbitals are different in H_2 and F_2 molecules, the bond strength and bond lengths differ between H_2 and F_2 molecules.
2. Pi (π)bonds are formed when two p_y or two p_z orbitals overlap laterally as shown below. It concentrates electron density between the nuclei, but above and below the internuclear axis:



Hybridization and Shapes of Molecules

Simple valence bond theory fails to explain the structure of molecules. For example, in a methane molecule (CH_4), if the covalent bonds between the hydrogen atoms and the carbon were formed by the overlap of 1*s* orbitals of four hydrogen atoms with the three 2*p* and one 2*s* orbitals of the carbon atom ($1s^22s^22p^2$), the H—C—H bond angles would be 90° for three of the hydrogen atoms and the fourth hydrogen atom would have a bond angle of 135°. Experimental evidence shows that all the bond angles in methane are 109.5° and the resulting shape is a regular tetrahedron. Thus, the formation of bonds by considering "pure" atomic orbitals cannot explain the different shapes observed in the molecules.

In 1931, L. Pauling proposed that the different atomic orbitals in the valence shell of the same atom combine or mix with each other resulting in more stable set of orbitals called hybridized orbitals. This process is known as **hybridization**.

Mathematically, the wave functions of the electrons in the orbitals of an atom are combined to give sets of equivalent wave functions called hybridized atomic orbitals. Hybridization is a simple mathematical process used for modifying electron densities, for describing bonding geometries and electron densities in more complex molecules. The driving force for hybridization is the formation of a bonding geometry with the lowest net potential energy, which is accessible by energetically feasible means.

Hybridization results in a set of atomic orbitals which have equal energies (degenerate) and are intermediate between those of the basic orbitals used to construct them. These hybridized atomic orbitals can overlap more effectively with the atomic orbitals of other atoms in the molecule, thus providing an overall molecular structure which has stronger bonds and lower energy. The other inner atomic orbitals which are not used in constructing the hybrid orbitals remain unaffected by the hybridization process.

The important characteristics of hybridization are:

1. The number of hybridized orbitals formed is equal to the number of atomic orbitals that get hybridized.
2. The hybridized orbitals are always equivalent in energy and shape.
3. The atomic orbitals involved in hybridization can be empty, half-filled or completely filled.
4. The hybridized orbitals have two lobes, one larger and one smaller; larger lobes are more effective in overlapping with other atomic orbitals and forming stable bonds. Smaller lobes are generally not shown since they are close to nucleus and do not effectively participate in bond formation.
5. The hybridized orbitals are directed in certain directions in space which will have stable arrangements. The type of arrangement gives the geometry of the molecule.
6. Hybridized orbitals are usually involved only in σ bonds; π bonds involve the overlap of unhybridized orbitals.
7. Hybridization is not involved in isolated atoms, only in covalent bond formation with other atoms.

However, it should be remembered that *hybridization is not a physical phenomenon*; it is merely a *mathematical operation* that combines the atomic orbitals in such a way that the new (hybrid) orbitals possess the geometric properties, etc., that are reasonably consistent with observations in a wide range (but not in all) of molecules. For example, the atomic orbitals of *s, p* and *d* types hybridize to give *sp*, sp^2, sp^3, sp^3d, sp^3d^2 type of hybridized atomic orbitals.

sp Hybridization

The hybridization of one *s* orbital and one *p* orbital on a central atom gives rise to two *sp* orbitals. The two hybridized *sp* orbitals, are in a linear arrangement, that is, 180° apart as shown in Figure 1.

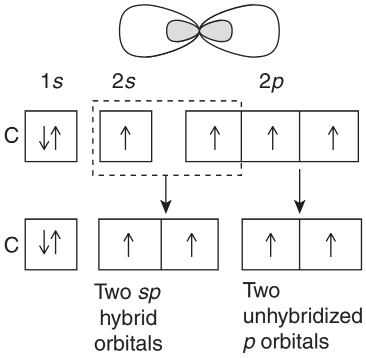


Figure 1 *sp* hybridization.

An example of *sp* hybridization is found in C_2H_2 (acetylene) and other alkynes with triple bonds. In this, the 2*s* orbital of each carbon atom mixes with only one of the three *p* orbitals, resulting in two *sp* orbitals while the other two *p* orbitals remain unchanged. The chemical bonding in acetylene then consists of the following:

1. Overlap between *sp*–*sp* hybridized orbital of the two carbon atoms forming a σ bond.
2. Lateral overlap of the two unhybridized *p* orbitals on one carbon atom with the respective *p* orbitals of the second carbon atom forming two π bonds.
3. Each carbon also forms a σ bond with a hydrogen by the overlap of its *sp* hybridized orbital with the *s* orbital of hydrogen: *s*–*sp* overlap at 180°.

The bonding in acetylene resulting from the overlap of orbitals is depicted in Figure 2.

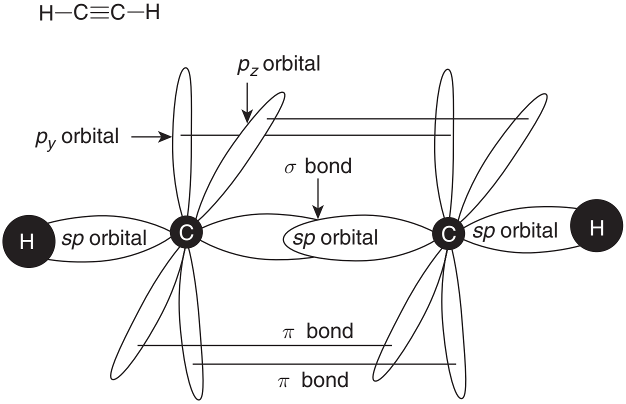


Figure 2 Bonding in CH≡CH.

Linear shape in molecules is basically due to *sp* type of hybridization. Another example of *sp* hybridization is BeH_2 molecule. The valence orbitals in Be, namely, 2*s*, 2*p* undergo *sp* hybridization to form two hybridized *sp* orbitals. The *overlap* between the hydrogen 1*s* orbitals and the two *sp*-hybrid orbitals of the beryllium constitutes the two Be—H "bonds" in this molecule (Figure 3).

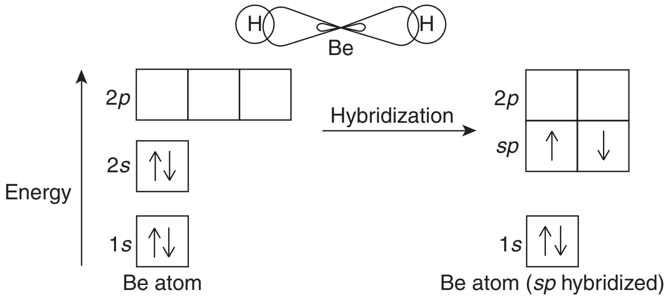


Figure 3 Bonding in BeH_2.

sp^2 Hybridization

The hybridization of one *s* orbital and two *p* orbitals of a central atom gives rise to three sp^2 orbitals (Figure 4). The three sp^2 hybridized orbitals are trigonal and planar, 120° apart.

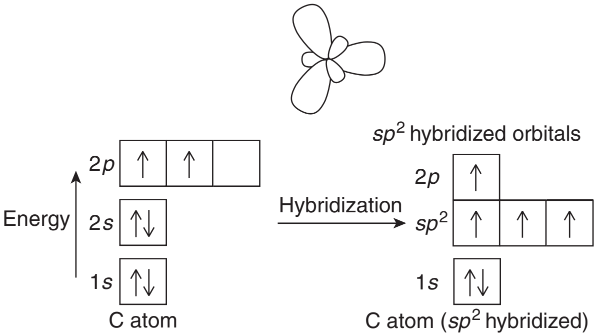


Figure 4 sp^2 hybridization.

For example, in ethene (C_2H_4), each carbon atom is sp^2 hybridized. Six sp^2 orbitals are generated (three from each carbon atom). One sp^2 orbital from each carbon atom overlaps with the other to form a σ bond between carbon atoms. The remaining two sp^2 orbitals of each carbon atom overlap with 1*s* orbitals of the two hydrogen atoms to produce four σ bonds. The unhybridized p_z orbital of each carbon atom forms a π bond by the parallel overlapping between two carbon atoms. The geometry of ethene molecule is trigonal in which the bonds are 120° apart (Figure 5).

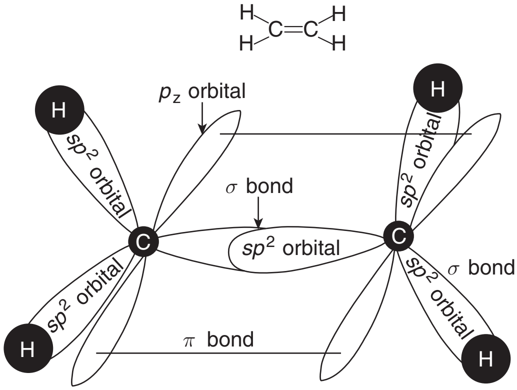


Figure 5 Bonding in $CH_2{=}CH_2$.

Other examples where sp^2 hybridization occurs are BF_3, CO_3^{2-}, and NO_3^-.

sp^3 Hybridization

Mixing of one *s* and all three *p* atomic orbitals produces a set of four equivalent sp^3 hybridized atomic orbitals. The four sp^3 hybrid orbitals having 75% *p*-character and 25% *s*-character point towards the vertices of a tetrahedron. Placement of the four orbitals in tetrahedral geometry provides the maximum separation between the electron pairs and minimizes electronic repulsion.

When sp^3 hybridized orbitals are used by the central atom in the formation of molecule, the molecule acquires the shape of a tetrahedron (Figure 6).

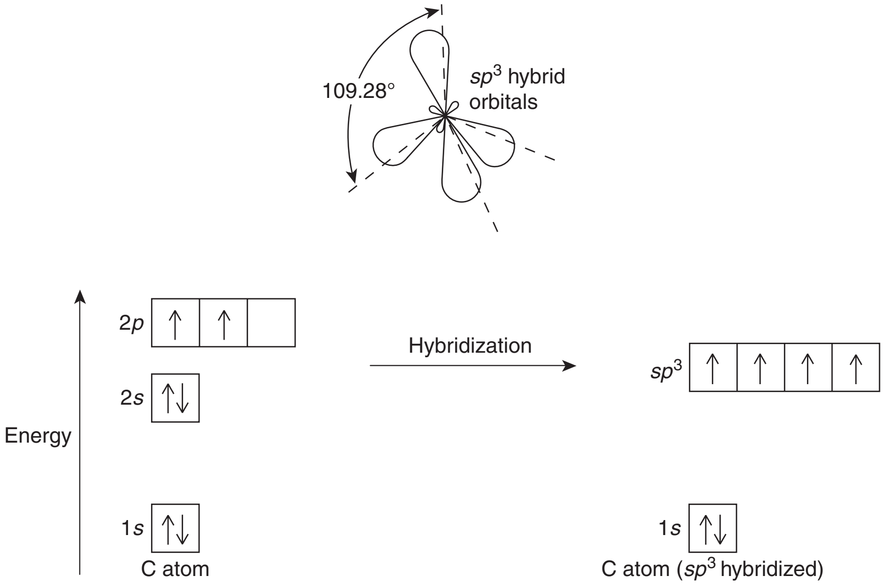


Figure 6 sp^3 hybridization.

An important example of this type of hybridization is methane, CH_4. In the free carbon atom, there are two unpaired electrons in separate 2*p* orbitals. The single 2*s*, and the three 2*p* orbitals of carbon mix into four sp^3 hybrid orbitals which are chemically and geometrically identical. The four sp^3 orbitals of carbon atom overlap with 1*s* orbitals of four hydrogen bonds to produce four σ bonds (Figure 7).

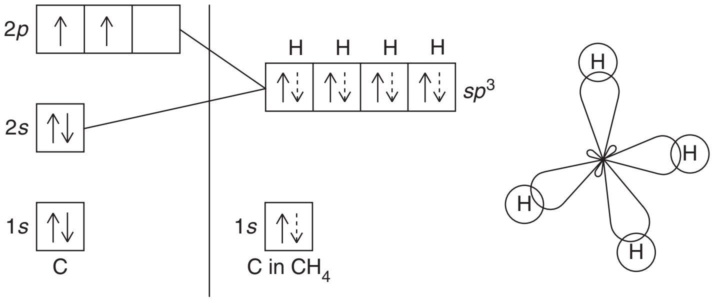


Figure 7 Bonding in CH_4.

Similarly, hybridization of one *s*, three *p* and one *d* atomic orbitals produce five sp^3d hybrid orbitals, which are trigonal bipyramidal in shape. Hybridization of one *s*, three *p* and two *d* atomic orbitals produces six sp^3d^2 hybridized orbitals which are octahedral–shaped (Figure 8).

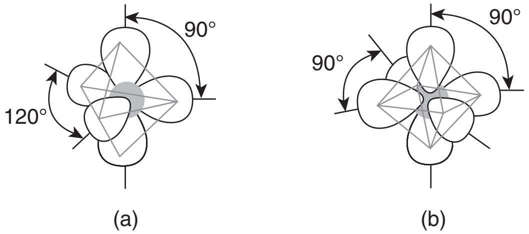


Figure 8 (a) Trigonal bipyramidal sp^3d hybridized orbitals; (b) octahedral sp^3d^2 hybridized orbitals.

For example, phosphorous in PCl_5 undergoes sp^3d hybridization and sulphur in SF_6 has sp^3d^2 hybridization (Figure 9).

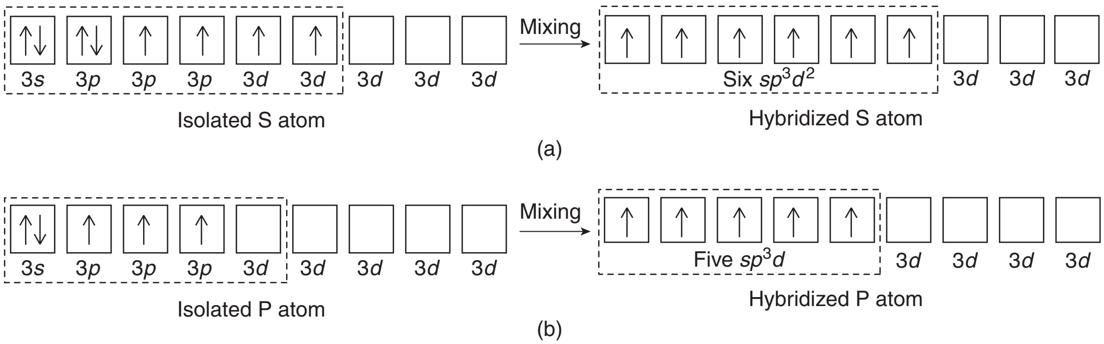


Figure 9 Hybridization of (a) sulphur atom in SF_6 and (b) phosphorous atom in PCl_5.

Lone Pair in Hybrid Orbitals

In the ammonia molecule, the nitrogen atom ($1s^22s^22p^3$) has three unpaired *p* electrons, but by mixing the one *s* and three *p* orbitals, four sp^3 hybrid orbitals are obtained. Three of the four sp^3 hybrid orbitals with one electron each form three shared electron bonds with three hydrogen atoms, resulting in formation of ammonia, NH_3. The fourth sp^3 hybrid orbitals contains the two remaining outer shell electrons which form a non-bonding lone pair. In acidic solutions, these can coordinate with a hydrogen ion, forming the ammonium ion NH_4^+. Although no bonds are formed by the lone pair in NH_3, these electrons give rise to a charge cloud that takes up space just like any other orbital.

In the water molecule, the oxygen atom ($1s^22s^22p^4$) forms four sp^3 orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two unpaired electrons are used for bonding (Figure 10).

The observed H—O—H bond angle in water (104.5°) and H—N—H bond angle is NH_3 (107.8°) is less than the tetrahedral angle (109.5°); because the non-bonding electrons tend to remain closer to the central atom and exert greater repulsion on the other orbitals, thus pushing the bonding orbitals closer together.

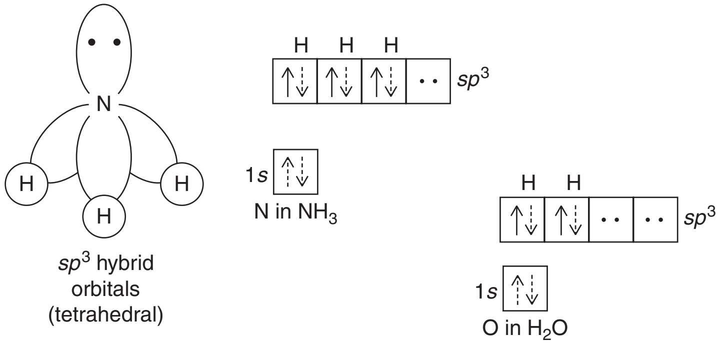


Figure 10 Hybridization in NH_3 and water.

Concept Check

- Who proposed the valence bond (VB) theory? What are the basic postulates of VB theory?
- Distinguish between σ and π bonds.
- What are the conditions to be satisfied by atomic orbitals to participate in hybridization?
- Explain the hybrization involved and predict the shape in the molecules: (a) XeF_2, (b) BCl_3 and (c) CCl_4.

2.2 Molecular Orbital Theory

Qualitative molecular orbital (MO) theory was introduced by Robert S. Mulliken and Friedrich Hund and a mathematical description was provided by Douglas Hartree and Vladimir Fock in 1930.

The molecular orbital theory proposes that all the atomic orbitals of the atoms involved in the covalent bond, combine to form new orbitals known as molecular orbitals which are associated with the molecule as a whole; while the valence bond theory considers only the valence electrons of atoms taking part in bonding and the inner atomic orbitals are left undisturbed. Two atomic orbitals of correct symmetry interact to form two molecular orbitals, while orbitals of incorrect symmetry do not overlap. The two molecular orbitals are formed by "addition" and "subtraction" of the wave function of the atomic orbitals. When the overlap occurs in the region where both the wave functions have the same sign, constructive interaction takes place and bonding molecular orbital is formed. If the overlap occurs in the region where the wave functions have opposite sign, destructive interaction takes place resulting in antibonding orbitals.

These molecular orbitals are quantized and assigned the symbols σ, π, δ, ϕ, … analogous to the atomic orbitals *s*, *p*, *d*, *f*, …. When the interaction occurs along the line joining the two nuclei, the resulting molecular orbital is called σ. When the overlap occurs in the regions directly above and below the line joining the nuclei, π molecular orbitals are obtained. The δ molecular orbitals are formed when the interaction occurs in all the four regions, that is, above, below and on both sides of line connecting the nuclei. The electrons of the original atomic orbitals of the bonding atoms then fill the molecular orbitals. The molecular orbital theory is based on the following assumptions:

1. When two atoms approach each other, their atomic orbitals lose their identity and mutually overlap to form new orbitals called molecular orbitals.
2. The molecular orbitals are polycentric and are associated with the nuclei of all the atoms constituting the molecule.

3. Only atomic orbitals of the same energy and same symmetry interact significantly.
4. The total number of molecular orbitals produced is always equal to the total number of atomic orbitals contributed by the atoms that have combined.
5. When two atomic orbitals overlap, they interact to form two molecular orbitals, in the following two ways:
   - When the atomic orbitals overlap in-phase, it leads to an increase in the intensity of the negative charge in the region of overlap; molecular orbital formed has lower potential energy than the separate atomic orbitals and is called a **bonding molecular orbital**.
   - When the atomic orbitals overlap out-of-phase, it leads to a decrease in the intensity of the negative charge between the nuclei and leads to higher potential energy; molecular orbital of this type are called **antibonding molecular orbitals**. Electrons in this type of molecular orbital destabilize the bond between atoms.

   The amount of stabilization of the bonding orbital equals the amount of destabilization of the antibonding orbital.
6. Electrons of the combining atoms are then assigned to these molecular orbitals. Each molecular orbital can accommodate a maximum of two electrons of successively higher energy according to Pauli's exclusion principle and Hund's rule of maximum multiplicity.

Linear Combination of Atomic Orbitals

One common mathematical approximation to generate molecular orbitals for some small diatomic molecules is called the linear combination of atomic orbitals (LCAO) approach. Consider two atoms A and B which have atomic orbitals described by the wave functions ψ_A and ψ_B. When the electron clouds of these two atoms overlap as the atoms approach, the wave function for the molecule can be obtained by a linear combination of the atomic orbitals ψ_A and ψ_B.

The atomic orbitals ψ_A and ψ_B combine to give rise to a pair of molecular orbitals ψ_g and ψ_u. The function ψ_g corresponds to increased electron density in between the nuclei due to in-phase overlap and is therefore a bonding molecular orbital. [$\psi_g = \psi_A + \psi_B$]. It is lower in energy than the original atomic orbitals. Function ψ_u corresponds to out-of-phase overlap and hence corresponds to minimized electron density in between the nuclei. This is an antibonding molecular orbital which is higher in energy [$\psi_u = \psi_A - \psi_B$].

Consider the simplest case of overlap of two atomic *s* orbitals from two individual atoms, which produces two molecular orbitals by their in-phase and out-of-phase overlap. In-phase or a constructive overlap of the two *s* orbitals leads to a bonding σ molecular orbital while the out-of-phase overlap leads to the antibonding σ^* molecular orbital as shown in Figure 11.

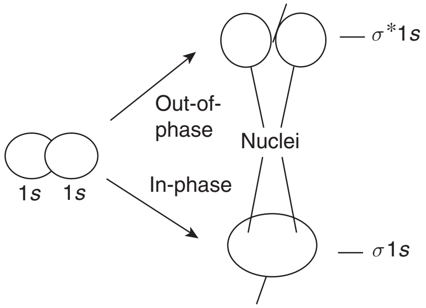


Figure 11 Bonding and antibonding molecular orbitals from overlap of two atomic *s* orbitals.

In the case of p orbitals, there are two different kinds of overlap possible, namely, end-on and side-on. End-on overlapping of two p_x atomic orbitals along the internuclear axis of the molecule creates σ (bonding) and σ^* (antibonding) molecular orbitals. While side-on overlap of p_y and p_z orbitals creates π (bonding) and π^* (antibonding) molecular orbitals.

The σ bonds are cylindrically symmetric to rotation about the bonding axis (the x-direction) while π bonds lack cylindrical symmetry and have a node passing through the bonding axis. The σ and π bonding and antibonding molecular orbitals formed from the overlap of two p atomic orbitals are shown in Figure 12.

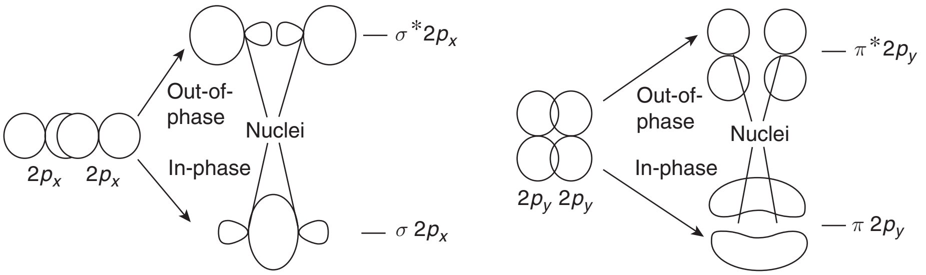


Figure 12 Bonding and antibonding molecular orbitals from overlap of two atomic p orbitals.

The molecular orbitals formed from the linear combinations of the atomic orbitals can thus be represented as shown in Table 1.

Table 1 Atomic and molecular orbitals

Atomic Orbitals	*Molecular Orbitals*
$1s_A + 1s_B$	$\sigma 1s$
$1s_A - 1s_B$	$\sigma^* 1s$
$2s_A + 2s_B$	$\sigma 2s$
$2s_A - 2s_B$	$\sigma^* 2s$
$2p_{xA} + 2p_{xB}$	$\sigma 2p_x$
$2p_{xA} - 2p_{xB}$	$\sigma^* 2p_x$
$2p_{yA} + 2p_{yB}$	$\pi 2p_y$
$2p_{yA} - 2p_{yB}$	$\pi^* 2p_y$
$2p_{zA} + 2p_{zB}$	$\pi 2p_z$
$2p_{zA} - 2p_{zB}$	$\pi^* 2p_z$

The order of the energy levels of these molecular orbitals is given as:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y \cong \pi 2p_z < \pi^* 2p_y \cong \pi^* 2p_z < \sigma^* 2p_x$$

These molecular orbitals are then filled with the total number of electrons (not just the valence electrons) counted by taking the atomic number of both the atoms of the covalent bond. The electrons are filled from the lowest energy orbital in the order of increasing energy and orbitals of equal energy are half-filled with parallel spin before they begin to pair up. Molecular orbital theory also predicts the bond order and hence the qualitative bond strength between covalently bonded atoms, which is given by:

$$\text{Bond order} = \frac{1}{2}(N_\mathrm{b} - N_\mathrm{a})$$

where N_b and N_a are the number of electrons in the bonding and antibonding molecular orbitals.

Furthermore, the MO theory has been very useful and successful in predicting the magnetic behavior of molecules. In filling up the molecular orbitals, if a molecule contains no unpaired electrons then it is diamagnetic and if it contains one or more unpaired electrons then it is paramagnetic. The diagram showing the relative energy levels of the combining atomic orbitals, the molecular orbitals formed from them and the order of filling up of the electrons is called the molecular orbital (MO) diagram. The orbitals of the individual combining atoms are written on either side of the diagram as horizontal lines at heights denoting their relative energies. The electrons in each atomic orbital are represented by arrows. The molecular orbitals of the molecule are represented in the middle of the diagram. Dashed lines connect the parent atomic orbitals with the molecular orbitals. For example the MO diagram for the simplest molecule, H_2, is shown in Figure 13.

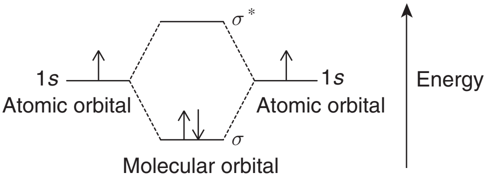


Figure 13 MO diagram of H_2.

The two hydrogen atoms with one electron each in 1*s* atomic orbitals combine to form $\sigma 1s$ (bonding) $\sigma^* 1s$ (antibonding) molecular orbitals; the two electrons fill a single bonding $\sigma 1s$ molecular orbital. The configuration of the H_2 molecule is written as $\sigma 1s^2$. As H_2 molecule has one electron pair in its bonding orbital and none in its antibonding orbital, molecular orbital theory predicts that H_2 has a bond order of 1 [(1/2) (2 – 0) = 1] and is diamagnetic as there are no unpaired electrons. Further applications of the molecular orbital theory to other simple diatomic molecules are discussed as follows.

Homonuclear Diatomic Molecules

The possible MO diagram for He_2 molecule is shown in Figure 14. It can be seen from the MO diagram that the configuration of He_2 is $(\sigma 1s)^2\ (\sigma^* 1s)^2$; the amount of stabilization due to filling of two electrons in bonding orbital is equal to the amount of destabilization due to the two electrons in antibonding molecular orbital. Therefore, there is no net stabilization due to bonding so the *He_2 molecule will not exist*. The bond order calculation also shows that the bond order is zero [(1/2) (2 – 2) = 0] for the He_2 molecule. The MO theory thus gives exactly the same prediction for He_2 as is observed – helium is a noble gas and does not form covalent compounds.

Relative Energy Levels of Molecular Orbitals of Li_2 and N_2

The study of the energies of electrons in molecules revealed that the relative energy levels of molecular orbitals of Li_2 to N_2 are different from those of O_2 and F_2. The explanation for the difference comes from

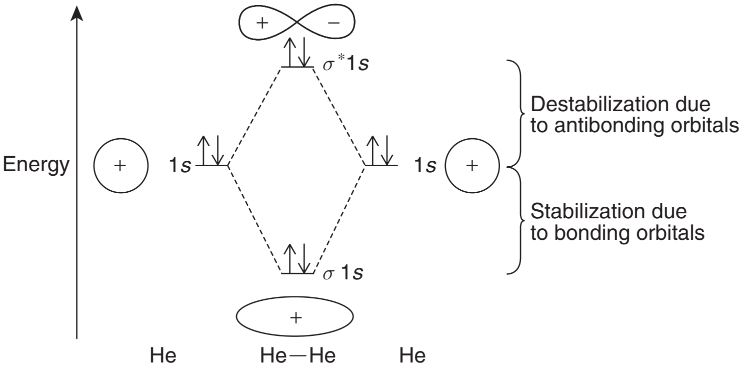


Figure 14 MO diagram of He_2.

the consideration of mixing of atomic orbitals. Because the *2s* and *2p* atomic energy levels for Li to N are relatively close and have less than half-filled *2p* orbitals, mixing occurs and causes the $\sigma^* 2s$ level to move down and the $\sigma 2p_x$ level to move up in energy. This process is called *sp* mixing. This effect causes the relative order of molecular orbitals to change, and a typical relative energy level diagram for Li_2, Be_2, B_2, C_2 and N_2 is shown in Figure 15.

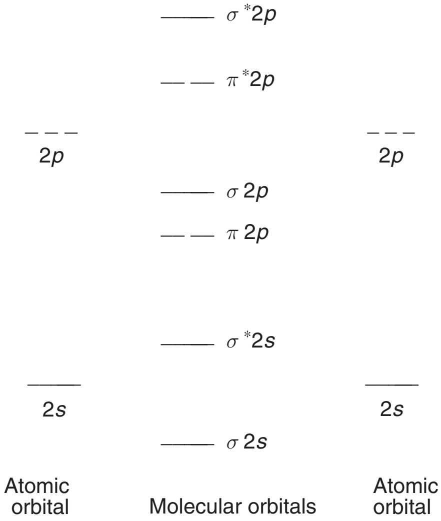


Figure 15 Relative energy levels of atomic and molecular orbitals in Li_2 to N_2 molecules.

The electronic configuration, the bond length and the bond energy of the molecules from Li_2 to F_2 are given below in Table 2. *KK* in the electronic configuration represents the closed *K* shell structure ($\sigma 1s^2\ \sigma^* 1s^2$). Note that B_2 and O_2 are paramagnetic due to the unpaired electrons in the molecular orbitals. Other molecules in this group are diamagnetic.

Table 2 Electronic configuration and bond energy (kJ/mol) from Li_2 to F_2

Molecule	*Electronic Configuration*	*Bond Energy*
Li—Li	$KK\ \sigma 2s^2$	110
Be—Be	$KK\ \sigma 2s^2\ \sigma^* 2s^2$	0 (Does not exist)
B—B	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_y^1\ \pi 2p_z^1$	290
C=C	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_y^2\ \pi 2p_z^2$	602
N≡N	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2$	942
O=O	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2\ \pi^* 2p_y^1\ \pi^* 2p_z^1$	494
F—F	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2\ \pi^* 2p_y^2\ \pi^* 2p_z^2$	155

Relative Energy Levels of Molecular Orbitals of O_2 and F_2

The 2*s* and 2*p* energy levels of O and F are very far apart. The three 2*p* orbitals of each O (or F) atom can form one σ and two π bonding and their corresponding antibonding molecular orbitals. The interaction of the 2*p* orbitals for the σ bond is stronger, and the levels of σ and antibonding σ orbitals are farther apart than those of π and antibonding π orbitals. Thus, the typical relative energy level diagram of O_2 and F_2 has the following arrangement as shown in Figure 16.

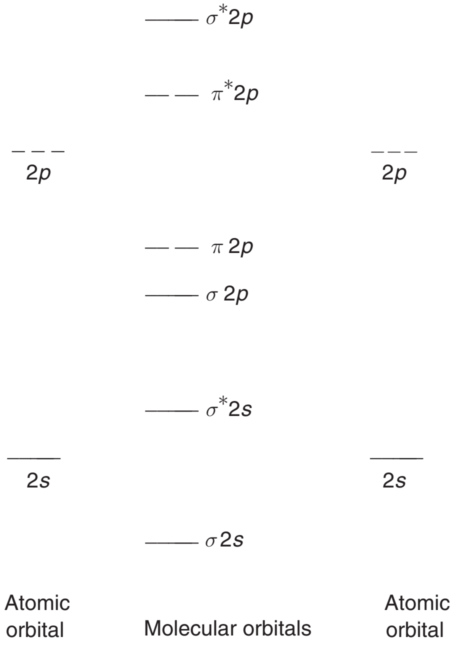


Figure 16 Relative energy levels of O_2 and F_2 molecules.

The electronic configuration for O_2 is:

$$\sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p^2\ \pi 2p^4\ \pi^* 2p^2$$

This electronic configuration indicates a bond order of 2, and the molecule can be represented by O=O. There is no net bonding from the $\sigma 2s$ orbitals, because the number of bonding electrons equals the number of antibonding electrons. The two electrons in $\pi^* 2p^2$ cancel two of the six bonding electrons ($\sigma 2p^2\ \pi 2p^4$). Therefore, there are four total bonding electrons. The two electrons in the $\pi^* 2p^2$ orbitals have the same spin, and they are responsible for the paramagnetism of oxygen. The MO diagram (Figure 17) and some related properties of the molecules B_2 to F_2 (Table 3) are given as follows:

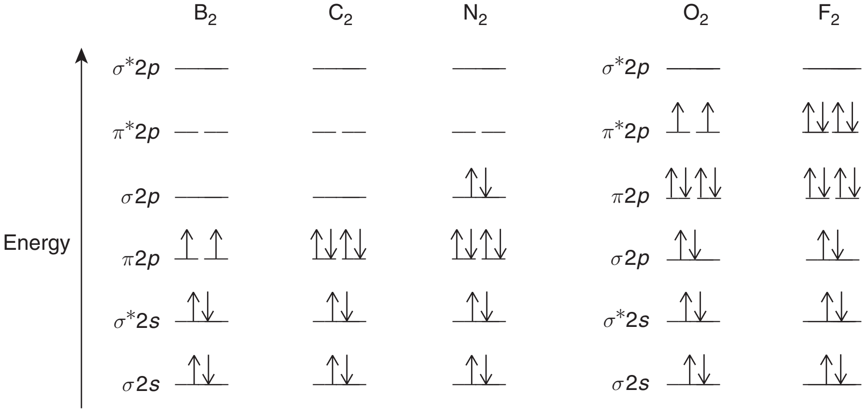


Figure 17 MO diagram of the molecules B_2 to F_2.

Table 3 Some properties of the molecules B_2 to F_2

Properties	*B_2*	*C_2*	*N_2*	*O_2*	*F_2*
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

Heteronuclear Diatomic Molecules

The MO theory can also be extended to heteronuclear diatomic molecules, that is, molecules that consist of two dissimilar atoms, such as HF, CO, NO, etc. The atomic orbitals of the two different atoms involved in bonding are now at different energy levels; the atom with higher electronegativity will have its atomic orbitals at lower energy, making larger contribution to the bonding molecular orbital. The atomic orbital with the higher energy makes a larger contribution to the antibonding molecular orbital. However, there is no interaction if the energy difference between orbitals is greater than 13 eV.

The electrons of the covalent bond in such molecules are no longer evenly shared between the two atoms, because it is energetically favorable for the electron pair to reside closer to one nucleus than to the other. This means that the chemical bond is polarized. For example, $H^{\delta+}—F^{\delta-}$ electron pair is located closer to the F nucleus than to the H nucleus.

The atomic orbitals in heteronuclear molecules combine together only if all the following conditions are satisfied:

1. They have the correct symmetry.
2. There is efficient overlap.
3. The orbitals are relatively close together in energy.

Heteronuclear diatomic molecules can have non-bonding orbitals, in addition to bonding and antibonding orbitals. Consider the following examples:

1. **HF molecule:** The atomic orbital energy levels are: hydrogen 1*s* (−13.61 eV), fluorine 2*s* (−40.17 eV) and 2*p* (−18.65 eV). In this case, there is no *s*-orbital interaction, because energy difference > 13 eV. The orbitals of 1*s* of hydrogen and $2p_x$ of fluorine can overlap to form a σ orbital due to compatible symmetry; while 1*s*, $2p_y$ and $2p_z$ of fluorine have no net overlap and are non-bonding. The MO diagram is as shown in Figure 18.

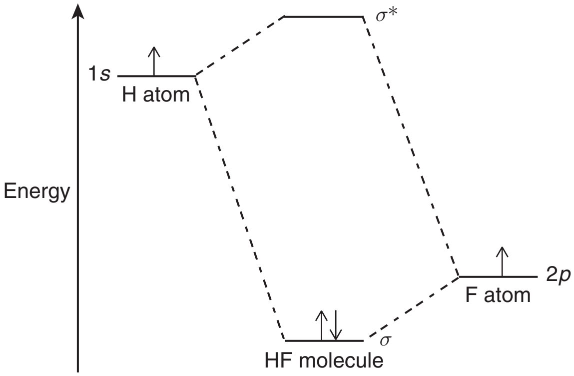


Figure 18 MO diagram of HF.

2. **Li—F molecule:** The electrons in the Li—F bond are quite close in energy to fluorine's 2*p* orbitals. The bonding molecular orbital is primarily obtained by the interaction 2*s* of lithium and $2p_x$ orbital of fluorine. The electrons in $2p_y$ and $2p_z$ orbitals on F that cannot bond with Li remain on F as lone pairs since fluorine is more electronegative than lithium. The electrons are more stable with lower energy, when they remain as lone pairs on fluorine rather than on lithium. So the MO diagram (Figure 19) predicts that the bond should be polarized towards fluorine.

   The construction of correlation diagrams of other heteronuclear diatomic orbitals follows exactly the same principles as those employed for LiF. The more electronegative element's orbitals are placed lower on the correlation diagram than those of the more electropositive element.

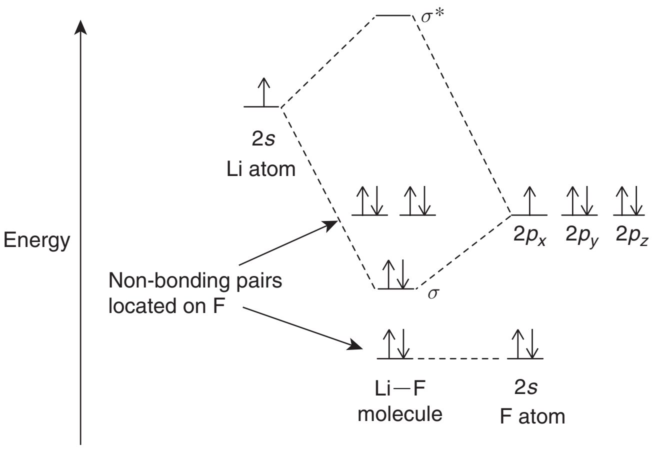


Figure 19 MO diagram of LiF.

3. **CO molecule:** The MO diagram (Figure 20) for the diatomic carbon monoxide (CO) shows that it is isoelectronic with nitrogen (N_2).

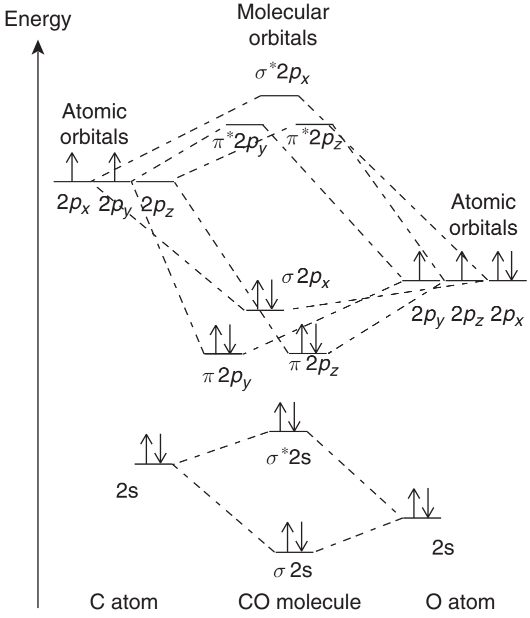


Figure 20 MO diagram of CO.

The heteronuclear diatomic ions such as cyanide ion, CN^-, and nitrosonium ion, NO^+, are also isoelectronic with nitrogen, N_2. The only difference in their MO diagrams lies in the relative energies of the orbitals.

Concept Check

- What are the molecular orbitals obtained by the linear combination of the atomic orbitals 1*s*, 2*s* and 2*p*? Give their increasing order of energy.
- Give the molecular orbital configuration and the bond order in the molecules N_2, F_2, CN^- and O_2^-.
- How does molecular orbital theory account for magnetic properties of molecules?

2.3 Metallic Bond

The theory of covalent bonding cannot be extended to explain the bonding mechanism in metals. This is because the individual atoms of a metal do not have enough valence electrons to share and form an octet. Thus, another theory was proposed to explain the force of attraction holding the atoms together in a piece of metal which is called the *metallic bond*. The metallic bond can account for most of the physical characteristics of metals such as strength, malleability (ability to be hammered into sheets), ductility (ability to be drawn into wires), luster and conductance of heat and electricity.

Theories of Metallic Bond

Various theories have been proposed to explain bonding in metals.

Electron Sea Model

In the case of metals, in which the valence electrons are not tightly bound to the nucleus, every atom achieves a more stable configuration by sharing the outer shell electrons with the various other atoms in the metal lattice. Quantum mechanically, atomic orbitals on all the atoms overlap to give a large number of molecular orbitals which extend over the whole metal. Hence, the valence electrons become detached from their parent atom and move freely amongst all the atoms within the crystal. In other words, the electrons are said to be *delocalized*. The metal lattice is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons. This is described as "an array of positive ions in a sea of electrons" (Figure 21).

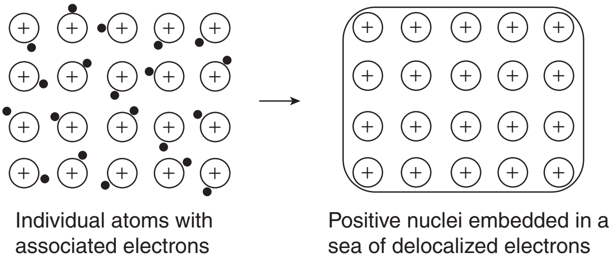


Figure 21 Electron sea model.

This theory of metallic bond successfully explains the observed physical characteristics of metals, such as strength, malleability, ductility, conduction of heat and electricity, and its metallic luster.

The strength of the metallic bond depends on the number of valence electrons contributed by the atoms to the delocalized electrons and the packing arrangement of the metal atom. More number of delocalized electrons and more closely packed atoms result in a stronger bond and a higher melting point. This explains why Group 1 metals have relatively low melting points compared to other metals. Since these metals have only one electron to contribute to the delocalized "sea" of electrons, are inefficiently packed and have large atomic radii, the delocalized electrons are farther away from the nucleus resulting in a weaker metallic bond.

The properties of the metals like malleability and ductility can be explained as the ability of the individual atoms to "slip" past one another, while being firmly held together by the electrostatic forces exerted by the electrons. As the electrons are delocalized over the positive ions and can move freely, metals exhibit good electrical conductivity. Heat conduction in metals can also be explained using same principle – the free electrons can transfer the energy at a faster rate than those which are covalently bonded having their electrons fixed in position.

Metals typically have a shiny, metallic luster because photons of light do not penetrate very far into the surface of a metal and are typically reflected, or bounced off from the metallic surface.

Band Theory or Molecular Orbital Theory

Molecular orbital theory may be extended to explain bonding in metals and is known as the band theory. Consider the example of a piece of sodium metal. Each sodium atom has single 3*s* valence electron. When two atoms are close together, the atomic orbitals will combine to form two molecular orbitals, $3\sigma$and $3\sigma^*$. The two electrons will occupy the bonding molecular orbital, while the antibonding orbital will remain empty. Similarly for three sodium atoms, three molecular orbitals are formed – bonding, non-bonding and antibonding. When four sodium atoms combine, we get two 3σorbitals and two $3\sigma^*$ orbitals. The quantum mechanical considerations do not permit these orbitals to be degenerate but they are closely placed, being almost similar in energy. The concept can be extended to *n* number of sodium atoms present in a piece of sodium metal. In this multi-atom system, the number of molecular orbital states will be equal to the number (*n*) of the atomic orbitals combining. Since the number of molecular orbitals is large, the spacing between them decreases to become almost negligible and we get a "band" of continuous energy levels (Figure 22). These molecular orbitals extend in all three dimensions over all the atoms in the metal piece.

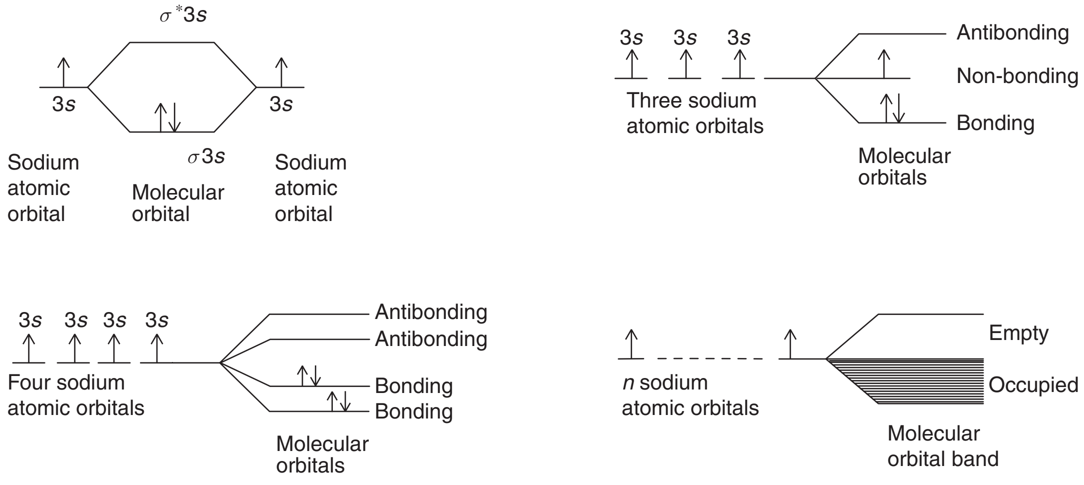


Figure 22 MO diagram for 2, 3, 4 and *n* sodium atoms.

The molecular orbital theory can explain most of the physical properties of metals. Since the energy levels are closely spaced, a very small amount of energy is required for the electrons to rise from filled orbitals to the unoccupied orbitals. The electrons have high degree of mobility and this explains the high electrical and thermal conductivity of metals. In presence of an electric field, the mobile electrons, which move in all directions in absence of a field, begin to move towards the anode, causing electric current to flow. Similarly when the metal is heated, the mobile electrons gain energy and move towards the colder part of the metal, thus transferring heat. The metallic luster arises because of absorption of light of any wavelength by metal atoms on the surface and its re-emission. The electrons absorb light, move to higher energy level and then emit the same amount of light to come back to the ground state. The presence of a band of energy levels in metals offers infinite number of such possible transitions between energy levels.

The band theory can also successfully explain the classification of materials into conductors, insulators and semiconductors. This results from the difference in the gap between the filled/partially filled valence band and the unfilled conduction band (Figure 23).

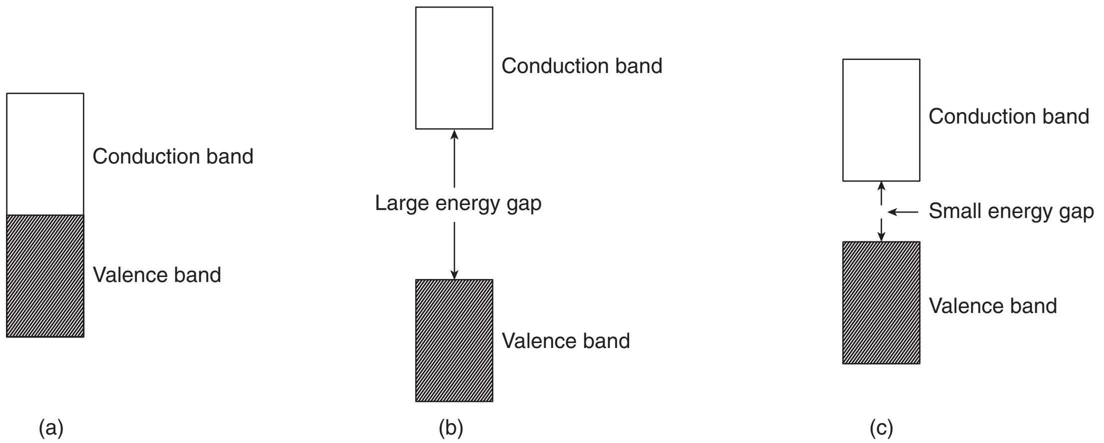


Figure 23 Valence and conduction band in (a) conductors, (b) insulators and (c) semiconductors.

1. In conductors, there is an overlap of valence and conduction bands; and the electrons from the valence band move effortlessly between the two bands. The electrons can thus move easily throughout the solid, making it a good conductor.
2. In insulators, the valence and conduction bands are widely separated and exist as distinct bands. The valence orbitals are filled so there is no movement of electrons possible, while the conduction band being empty, there are no electrons to move. Also, due to difference in the energy gap, a large amount of energy is required to promote the electrons from valence band to conduction band. So effectively there are no mobile charge carriers and hence insulators or non-metals do not conduct electricity.
3. In semiconductors, the valence and conduction bands are so placed that some amount of electrons can be excited to the upper vacant conduction band. Only a moderate amount of energy is required to promote electrons from the filled valence band to the empty conduction band. Semiconductors thus conduct electricity with some input of external energy. Also, since increase in temperature will increase the promotion of electrons to the conduction band, the conductivity of semiconductors increases with increase in temperature. Another way of increasing conductivity of semiconductors is through doping.

Concept Check

- What is the theory proposed to explain the bonding in metals?
- How does the theory for metallic bonding explain the following properties of metals: Luster, malleability and conductivity?

Key Terms

Valence bond theory
Hybridization
Geometry of molecules
Molecular orbital theory
Bonding and antibonding molecular orbitals
Molecular orbital diagram
Linear combination of atomic orbitals
Sigma (σ) and pi (π) bonds
Metallic bond

Objective-Type Questions

Multiple-Choice Questions

1. Linear shape in molecules is basically due to
   - **a.** *sp* hybridization.
   - **b.** sp^2 hybridization.
   - **c.** sp^3 hybridization.
   - **d.** none of the above.
2. Which of the following molecules involve sp^2 hybridization?
   - **a.** BeH_2
   - **b.** BF_3
   - **c.** PCl_5
   - **d.** SF_6
3. Phosphorous in PCl_5 undergoes:
   - **a.** sp^3 hybridization.
   - **b.** sp^3d hybridization.
   - **c.** sp^3d^2 hybridization.
   - **d.** none of the above.
4. What is the shape of sp^3d^2 hybridized orbitals?
   - **a.** trigonal
   - **b.** tetrahedral
   - **c.** trigonal bipyramidal
   - **d.** Octahedral
5. Which of the following pairs is isoelectronic?
   - **a.** N_2 and O_2
   - **b.** NO^+ and N_2
   - **c.** B_2 and C_2
   - **d.** None of these.
6. Which of the following pairs is isoelectronic?
   - **a.** N_2 and CO
   - **b.** O_2^- and N_2
   - **c.** Li_2 and Be_2
   - **d.** None of these.
7. Which among the following will have the longest bond length?
   - **a.** O_2^+
   - **b.** O_2
   - **c.** O_2^-
   - **d.** O_2^{2-}
8. Which among the following is paramagnetic?
   - **a.** N_2
   - **b.** O_2
   - **c.** O_2^{2-}
   - **d.** H_2

9. Which among the following will have the highest bond order?
   a. N_2
   b. N_2^+
   c. N_2^-
   d. N_2^{2-}

10. The bond order of O_2^+ molecular ion is
   a. 1
   b. 2
   c. 2.5
   d. 3

11. Which of the following configurations corresponds to paramagnetic property?
   a. $\sigma 2s^2$
   b. $\sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2$
   c. $\pi 2p_y^2$
   d. $\pi^* 2p_y^1\ \pi^* 2p_z^1$

12. Which of the following is true for energy of antibonding orbitals?
   a. It is greater than the energy of atomic orbitals.
   b. It is lower than energy of bonding orbitals.
   c. It is same as energy of bonding orbitals.
   d. It is lower than the energy of atomic orbitals.

Fill in the Blanks

1. Number of electrons in antibonding molecular orbitals of NO^- is _______.

2. The bond order on O_2^- is _______ than that in O_2 which in turn is _______ than that in O_2^+ .

3. Bond length of a molecule is _______ proportional to the bond order, whereas bond energy is _______ proportional to bond order.

4. The most stable amongst the following O_2, O_2^+, O_2^-, O_2^{2-} is _______.

5. The carbon atom in C_2H_6 is _______ hybridized.

Review Questions

Short-Answer Questions

1. State the postulates of valence bond theory explaining the formation of strong covalent bonds.

2. Explain the hybridization involved in BF_3 and predict its shape.

3. Explain *sp* hybridization with examples.

4. What are the shapes of PCl_5 and SF_6?

5. Explain with example, the role of lone pair of electrons in determining the shape of the molecules.

6. What conditions must be fulfilled for LCAO?

7. Why H_2^+ ion is more stable than H_2^- ion though both of them have the same bond order.

8. With the help of MO theory, show that Ne_2 cannot exist as a stable species.

9. Arrange the following in increasing order of O – O bond length: O_2, KO_2, Na_2O_2.

10. Arrange O_2, O_2^+, O_2^-, O_2^{2-} in order of decreasing stability.
11. What are the bond orders of H_2 and H_2^+?
12. Hydrogen forms a diatomic molecule while helium does not. Explain.
13. Why are metals good conductors of electricity?
14. What is hybridization? What are the properties of hybrid orbitals?
15. What are the basic postulates of molecular orbital theory in explaining the bonding between atoms?
16. What are bonding and antibonding molecular orbitals?
17. Most metals are found to have a regular compact crystalline structure. Explain why?
18. What is the free electron (electron sea) theory of metallic bonding? How does it account for metallic luster?
19. Explain conductors and insulators on the basis of band theory.

Long-Answer Questions

1. Explain why the dissociation energy of N_2 is higher than N_2^+, while that of O_2 is lower than O_2^+.
2. Write the MO configuration of the diatomic molecule of the element with atomic number 9. Calculate its bond order and predict its magnetic behavior.
3. Explain why O_2 is paramagnetic while F_2 is diamagnetic and compare the bond lengths of N_2 and N_2^+.
4. Write down the molecular orbital electronic configuration for B_2 and B_2^+ and compare the bond length and predict their magnetic property.
5. Write down the molecular orbital electronic configuration for O_2 and O_2^-. Compare the bond length and predict their magnetic property.
6. Write down the MO configuration for O_2 and N_2. Compare their bond length and magnetic properties.
7. Molecular oxygen is paramagnetic substance. Explain it.
8. How does molecular orbital theory explain the difference in the reactivity of N_2, O_2 and F_2.
9. A gas consisting of X_2 molecules is found to be paramagnetic. What pattern of molecular orbital must apply in this case?
10. **a.** What is hybridization?
    b. What are *sp*^{2} and *sp*^{3} hybridizations? Explain with examples.
11. **a.** Draw the molecular orbital diagram for O_2 molecule.
    b. Write the electronic configuration, calculate the bond order and predict the magnetic behavior of: O_2, O_2^+, O_2^-, O_2^{2-}.
12. **a.** Draw the molecular orbital diagram for NO molecule.
    b. Write the electronic configuration, calculate the bond order and predict the magnetic behavior of NO, NO^+, NO^-.
13. How and why are the molecular orbital diagrams of nitrogen (N_2) and oxygen (O_2) molecules different? What are the implications?

14. What is the band theory for metallic bonding? How does it explain the categorization of metals into conductors, insulators and semiconductors?

15. Discuss the electron sea model (free electron theory) for metallic bonding. How does it account for: (a) thermal conductivity and (b) metallic luster.

16. What is metallic bond? Explain it on the basis of molecular orbital theory.

Answers

Multiple-Choice Questions

1. (a)
2. (b)
3. (b)
4. (d)
5. (b)
6. (a)
7. (d)
8. (b)
9. (a)
10. (c)
11. (d)
12. (a)

Fill in the Blanks

1. 6
2. less, less
3. inversely, directly
4. O_2^+
5. sp^3

3 Spectroscopy

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Different types of electromagnetic radiations.
- Electromagnetic spectrum.
- Beer–Lambert's law and its applications.
- Basic principle, instrumentation and applications of UV–visible, infrared and microwave spectroscopy.

3.1 Introduction

The study of properties, composition and structure of matter by interaction of electromagnetic radiations is called **spectroscopy**. The interaction of electromagnetic radiation with the matter may occur in two different ways.

1. The matter may absorb a portion of monochromatic electromagnetic radiation. In such a case, it is called **absorption spectroscopy**.
2. In **emission spectroscopy**, matter undergoes a transition from a state of high energy to a state of lower energy by emitting excess energy in form of radiation.

Absorption or emission of electromagnetic radiation takes place by the molecules or by the atoms. When it occurs by the atoms, the spectroscopy is called **atomic spectroscopy**. On the other hand it is called **molecular spectroscopy**, if the absorption or emission of electromagnetic radiation takes place by molecules. In this chapter, a few aspects of molecular spectroscopy are discussed.

3.2 Electromagnetic Radiations

Electromagnetic radiations are considered as the waves of energy propagated from a source in space, containing oscillating electric and magnetic fields perpendicular to each other. Different electromagnetic radiations are: Cosmic rays, γ-rays, X-rays, ultraviolet (UV) radiations, visible radiations, infrared (IR) radiations, microwaves and radio waves.

Some of the important characteristics of electromagnetic radiations are as follows:

1. These are generated by fluctuation or oscillation of electric and magnetic fields, which are perpendicular to each other and are coplanar as shown in Figure 1.

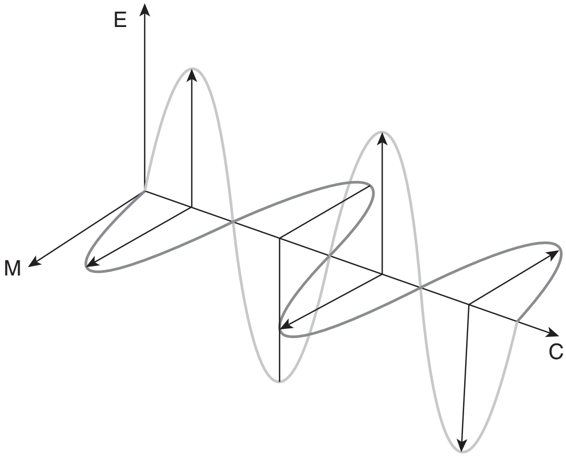


Figure 1 Planes of electromagnetic waves.

2. These propagate through space in form of waves.
3. These do not require any medium for propagation.
4. All electromagnetic radiations travel with the velocity same as that of light (i.e., 3×10^8 m/s).
5. Each kind of radiation has a definite range of wavelength and hence frequency. These are given in Table 1.

Table 1 Different electromagnetic radiations with their wavelength range

Name of Electromagnetic Radiation	*Wavelength Range*
Gamma Rays	100 to 1 pm
X-rays	10 nm to 100 pm
Ultra Violet	100 to 400 nm
Visible	400 to 800 nm
Infrared	0.75 to 1000 μm
Microwave	0.1 to 50 cm
Radio wave	1 to 30000 m

6. The energy of electromagnetic radiation is directly proportional to frequency (ν) or is inversely proportional to wavelength (λ). It can mathematically be given as:

$$E \propto \nu \tag{3.1}$$

or

$$E = \mathrm{h}\nu \tag{3.2}$$

or

$$E = \frac{\mathrm{h}c}{\lambda} \tag{3.3}$$

where E is the energy of radiation, h is Planck's constant and c is the velocity of light.

Electromagnetic Spectrum

Electromagnetic radiations differ from one another in terms of wavelength and frequency. When these radiations are arranged in increasing order of their wavelength or decreasing order of frequencies, the pattern obtained is called **electromagnetic spectrum** (Figure 2). Different electromagnetic radiations can be arranged in increasing order of their wavelength or decreasing order of frequencies as follows.

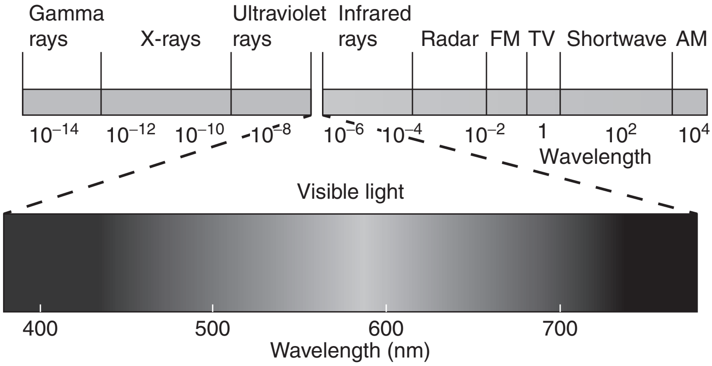


Figure 2 Electromagnetic spectrum.

3.3 Laws of Absorption

When a monochromatic electromagnetic radiation is passed through a substance or its solution, a portion of it is absorbed and the rest are transmitted. Absorbed electromagnetic radiation brings a change in electronic, vibrational and rotational energy levels of the molecules of the substance. The change in electronic energy levels is induced by ultraviolet and visible radiations, whereas infrared and microwave radiations bring about the change in vibrational and rotational energy levels. The energy difference between any two consecutive electronic energy levels ($\Delta E_{\text{electronic}}$) is greater than that between any two consecutive vibrational energy levels ($\Delta E_{\text{vibrational}}$) which is in turn greater than that between any two consecutive rotational energy levels ($\Delta E_{\text{rotational}}$).

The absorption of electromagnetic radiation by the molecules is governed by Beer–Lambert's law which is discussed as follows.

Beer–Lambert's Law

Beer–Lambert's law states that when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease in intensity of incident radiation with thickness of absorbing solution is proportional to the product of the intensity of incident radiation and concentration of the solution. It can be expressed mathematically as

$$-\frac{\mathrm{d}I}{\mathrm{d}x} \propto IC \tag{3.4}$$

where $-\mathrm{d}I$ is the decrease in intensity with respect to thickness of the solution $\mathrm{d}x$, I is the intensity of incident radiation and C is the concentration of the solution in moles/liter.

Equation (3.4) can be written as:

$$-\frac{\mathrm{d}I}{\mathrm{d}x} = kIC$$

$$\frac{\mathrm{d}I}{I} = -kC\mathrm{d}x \tag{3.5}$$

Let I_0 be the intensity of radiation before entering into the absorbing solution (i.e., intensity of incident radiation). Let I be the intensity of radiation after passing through the absorbing solution of thickness x cm (i.e., intensity of transmitted radiation). Then integrating Eq. (3.5), between these limits, we get

$$\int_{I_0}^{I} \frac{\mathrm{d}I}{I} = -kC\int_{0}^{x} \mathrm{d}x$$

$$\ln\frac{I}{I_0} = -kCx \tag{3.6}$$

where x is the thickness of solution or path length or diameter of the cell, k is the constant of proportionality and I/I_0 is transmittance (T). Thus, **transmittance** is the ratio of intensity of transmitted radiation (I) to that of incident radiation (I_0).

Equation (3.6) can also be written as

$$2.303\ \log\frac{I}{I_0} = -kCx$$

$$\log\frac{I}{I_0} = -\frac{kCx}{2.303}$$

$$\log\frac{I_0}{I} = \frac{k}{2.303}Cx$$

or

$$\log\frac{I_0}{I} = \in Cx \tag{3.7}$$

where $\in$ is called molar absorption coefficient or molar absorptivity or molar extinction coefficient and $\log I_0/I$ is called **absorbance** or **optical density** (A).

Hence, Eq. (3.7) can be written as

$$\mathrm{A} = \in Cx \tag{3.8}$$

Equation (3.8) is the simplest form of Beer–Lambert's Law.

Again,

$$A = \log\frac{I_0}{I} = -\log\frac{I}{I_0}$$

or

$$A = -\log T \tag{3.9}$$

where T is the transmittance of the solution.

Equation (3.7) can also be written as

$$\frac{I_0}{I} = 10^{\in Cx} \tag{3.10}$$

where I_0/I is called **opacity**.

If concentration and thickness of absorbing solution become unity (i.e., $C = 1$ mol/L and $x = 1$ cm), then Eq. (3.8) will become

$$A = \in \tag{3.11}$$

Thus, **molar absorption coefficient** ($\in$) can be defined as the absorbance (A) of an absorbing solution of unit concentration and unit path length.

Equation (3.8) can be given by

$$\in = \frac{A}{Cx} = \frac{\log(I_0 / I)}{Cx}$$

Molar absorption coefficient depends on the frequency of incident radiation and is the largest when absorption of radiation takes place to a greater extent. Its dimensions are

$$\frac{1}{\text{concentration} \times \text{length}}$$

and it is normally expressed as L/mol/cm or dm^3/mol/cm.

Considering 1 L = 10^3 cm^3, $\in$ can be expressed as cm^2/mol and may be regarded as a molar cross section for absorption. Greater the cross-sectional area of absorbing solution, higher is the ability of molar absorption coefficient to block the passage of the incident radiation.

Application

Concentration of a solution of a substance can be determined by using this law. At first, a standard solution (whose concentration C_1 is known) of that substance is prepared. Its absorbance can be determined by following relation.

$$A_1 = \in C_1 x \tag{3.12}$$

The absorbance of the solution, whose concentration (C_2) is to be determined, can be given by:

$$A_2 = \in C_2 x \tag{3.13}$$

Dividing Eq. (3.12) by Eq. (3.13), we get

$$\frac{A_1}{A_2} = \frac{\in C_1 x}{\in C_2 x}$$

$$\frac{A_1}{A_2} = \frac{C_1}{C_2} \tag{3.14}$$

$$C_2 = \frac{C_1}{A_1} \times A_2$$

The values of A_1 and A_2 can be obtained from spectrophotometer. Putting the values of A_1, A_2 and C_1, concentration of the solution (C_2) is determined.

Problem 1

A solution shows a transmittance of 10%, when taken in a cell of 2.5 cm thickness. Calculate the concentration if the molar absorption coefficient is 12,000 dm^3/mol/cm.

Solution

Given that:

$$\frac{I}{I_0} = \frac{10}{100}$$

so,

$$\frac{I_0}{I} = 10$$

Also given that thickness of the cell (x) = 2.5 cm, and molar absorption coefficient ($\in$) = 12,000 dm^3/mol/cm.

According to Beer–Lambert's law,

$$\log\frac{I_0}{I} = \in Cx$$

or

$$\log 10 = 12{,}000 \times C \times 2.5 \Rightarrow C = \frac{1}{12000 \times 2.5}$$

or

$$C = \frac{1}{30} \times 10^{-3} = 0.333 \times 10^{-4}$$

Hence concentration of the solution is 0.333×10^{-4}mol/L.

Problem 2

If the molar absorption coefficient of a colored complex is 3.45×10^4 dm^3/mol/cm at 300 nm, calculate the absorbance of a 4.5×10^{-6} M solution in 70 mm cell when measured at this wavelength.

Solution

Given that:

Molar absorption coefficient ($\in$) = 3.45×10^4 dm^3/mol/cm.

Concentration of the solution = 4.5×10^{-6} M.

Thickness of the cell (x) = 70 mm = 70×10^{-1} cm.

According to Beer–Lambert's law,

$$A = \in Cx$$

Substituting the values of $\in$, C and x in the above expression, we get

$$A = 3.45 \times 10^4 \times 4.5 \times 10^{-6} \times 70 \times 10^{-1}$$

$$= 108.675 \times 10^{-2}$$

Hence, absorbance of the solution is 108.675×10^{-2}.

Concept Check

- What is transmittance of a solution?
- Derive the relation between energy and wave length of a radiation.
- What do you mean by absorbance of a solution?
- Differentiate between incident radiation and transmitted radiation.
- The transmittance of an aqueous solution is 20% at 25°C and 350 nm, for a 4×10^{-4}M solution in a 3 cm cell. Calculate the molar extinction coefficient.

3.4 Ultraviolet–Visible Spectroscopy

Radiations with wavelength (λ) range 200–800 nm correspond to the ultraviolet and visible regions of electromagnetic spectrum. Radiations possessing wavelength in 100–200 nm range fall in far UV or vacuum UV region. Hydrogen discharge lamp or deuterium discharge lamp or tungsten filament lamp is used as source to generate ultraviolet and visible radiations.

Basic Principle

Electrons remain in different molecular orbitals in molecules. These molecular orbitals are: sigma bonding molecular orbital (σ), pi bonding molecular orbital (π), non-bonding molecular orbital (n), pi antibonding molecular orbital (π^*) and sigma antibonding molecular orbital (σ^*). They possess different energies. These orbitals can be arranged in increasing order of energy as shown in Figure 3.

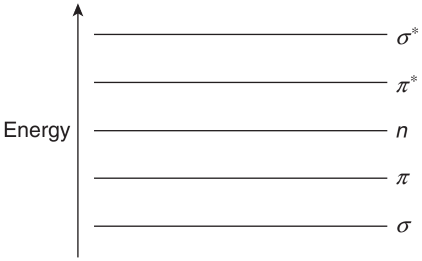


Figure 3 Energy level diagram for different molecular orbitals.

When a beam of monochromatic UV–visible radiation is made incident on a sample, a portion of that is absorbed. As a result of this, electrons are excited to higher energy level or antibonding molecular orbital. This excitation of electrons is known as **electronic transition**. Different possible transitions are:

$$\sigma \text{ to } \sigma^*(\sigma \rightarrow \sigma^*), n \text{ to } \sigma^*(n \rightarrow \sigma^*), \pi \text{ to } \pi^*(\pi \rightarrow \pi^*) \text{ and } n \text{ to } \pi^*(n \rightarrow \pi^*)$$

These are depicted in Figure 4.

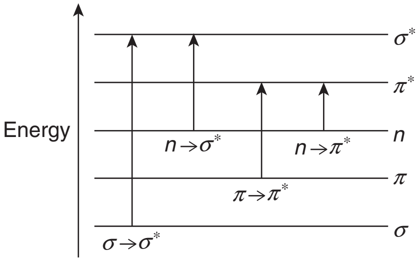


Figure 4 Relative energies required for various electronic transitions.

The energy required for different electronic transitions obey the following order:

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

The characteristic features of these electronic transitions are discussed as follows:

1. **$\sigma\rightarrow \sigma^*$ transition**
   When an electron present in σ bonding molecular orbital, jumps to σ^* antibonding molecular orbital, the transition is called $\sigma \rightarrow\sigma^*$ transition. Molecules such as methane, ethane, etc. containing only σ bonds show this type of transition. Since σ bonds are stronger, radiations with higher energy (shorter wavelength) can cause this transition. Radiation with this wavelength range fall beyond normal UV region, hence, radiation from far UV region (below 200 nm) is required for $\sigma \rightarrow \sigma^*$ transition. For example saturated hydrocarbons such as methane, propane, etc. absorb radiation of wavelength about 150 nm.

   Usual spectroscopic technique cannot be used below200 nm, since oxygen present in air absorb radiation of this wavelength range. In order to carry out $\sigma \rightarrow \sigma^*$ transition, the equipment should be placed in vacuum. Since, radiation below 200 nm is used in vacuum, this wavelength region is called **vacuum UV region**.
2. **$n \rightarrow\sigma^*$ transition**
   The $n \rightarrow\sigma^*$ transition results from the excitation of a non-bonding electron into σ^* antibonding orbital. This type of transition occurs in saturated compounds containing a hetero atom, which possesses non-bonding electron pairs or lone pair of electrons. Alkyl halides like methyl chloride (CH_3Cl), alcohols like methyl alcohol (CH_3OH), alkyl amines like methyl amine (CH_3NH_2), etc., show this type of transition. This transition requires less energy than that required for $\sigma \rightarrow \sigma^*$ transitions.

   Methyl chloride (CH_3Cl) absorbs radiation of wavelength 175 nm (high energy) whereas absorption occurs for methyl iodide (CH_3I) at 258 nm (less energy). It is because non-bonding electrons or lone pair of electrons on iodine (I) are loosely held due to larger size as compared to chlorine (Cl). Molar extinction coefficient ($\in$) for CH_3I is also greater than that for CH_3Cl because greater the probability of a particular transition, greater is the value of its molar extinction coefficient.
3. **$\pi \rightarrow \pi^*$ transition**
   Energy required for this transition is less than that required for $n \rightarrow\sigma^*$ transition. This type of transition occurs in the compounds which contain multiple bonds (double or triple bonds). Alkenes such as ethylene ($CH_2=CH_2$), alkynes such as acetylene ($CH\equiv CH$) and aromatic compounds like benzene undergo this type of transition.

   In this transition, electron present in π bonding molecular orbital is excited to π^* antibonding molecular orbital. This excitation requires less energy and hence occurs in longer wavelength, which corresponds to normal ultraviolet region of electromagnetic spectrum.

4. **$n \rightarrow \pi^*$ transition**

   In this case non-bonding electron is excited to π^* antibonding molecular orbital. This type of transition requires less energy as compared to that required for $\pi \rightarrow \pi^*$ transition. Compounds containing multiple bonds and hetero atoms such as O, N, S, etc., which carry lone pair of electrons show this type of transition. Such compounds are aldehydes, ketones, etc. Aldehydes and ketones which do not have carbon–carbon multiple bonds, absorb radiation of wavelength range 270–300 nm to undergo $n \rightarrow \pi^*$ transition. On the other hand, carbonyl compounds having conjugate double bond (alternate double bonds) absorb in the range of 300–350 nm.

   Compounds containing specific groups absorb UV–visible radiation of definite wavelength to undergo different electronic transitions. For example, carbonyl group ($>C=O$) absorbs at 180 nm which corresponds to $\pi \rightarrow \pi^*$ transition and at 285 nm indicating $n \rightarrow \pi^*$ transition. Such groups are called chromophores. Thus, **chromophore** is an isolated covalently bonded group that shows characteristic absorption in ultraviolet and visible regions.

There are some other groups which do not show a characteristic absorption in UV–visible region but their presence with a chromophore brings about a shift in absorption band towards longer wavelength (red end). Such groups are called **auxochromes** and the shift in absorption band towards longer wavelength is called **bathochromic shift** or **red shift**. Some common auxochromic groups are –OH, –OR, $-NH_2$, etc. The effect of auxochrome is due to its ability to extend the conjugation of a chromophore by sharing of nonbonding electrons. For example, benzene (C_6H_6) shows absorption at 255 nm whereas aniline ($C_6H_5–NH_2$) absorbs at 280 nm. This shift in absorption towards longer wavelength is due to presence of $-NH_2$ group, which is an auxochrome. Shift of absorption band towards red end also occurs by change of solvent.

The absorption band may shift towards shorter wavelength due to removal of conjugation and change of solvent. This shift of absorption band towards shorter wavelength is called **hypsochromic shift** or **blue shift**. For example, absorption maximum occurs at 280 nm, in case of aniline due to the conjugation of non-bonding electrons on nitrogen atom of $-NH_2$ group with the π-electron system of benzene ring. This absorption band of aniline occurs at ~203 nm, when it is subjected to acidic hydrolysis or acidic solution. It is because aniline is converted to anilinium ($C_6H_5 - \overset{+}{N}H_3$) ion in acidic solution and conjugation is removed due to absence of non-bonding electron pair on N–atom of $-NH_2$ group.

Instrumentation

The instrument used in UV–visible spectroscopy is called **UV–visible spectrophotometer**. The block diagram for UV–visible spectrophotometer is shown in Figure 5.

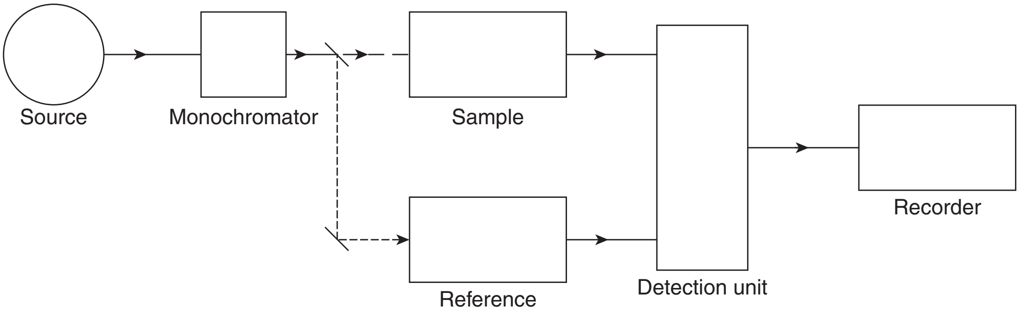


Figure 5 Block diagram for UV–visible spectrophotometer.

Different components of the spectrophotometer are discussed as follows:

1. **Source:** It produces UV–visible radiation, which is allowed to pass through monochromator.
2. **Monochromator:** It allows a monochromatic radiation which is divided into two beams of equal intensity.
3. **Sample and reference cells:** These are made up of quartz or fused silica. One beam of selected monochromatic radiation is passed through the sample cell and the other beam of equal intensity is passed through the reference cell.
4. **Detection unit:** The sample absorbs radiation and its intensity is lowered. Thus, an intense beam from reference cell and a weak beam from the sample cell is received in the detection unit. As a result, an alternating current is generated and is amplified in this unit.
5. **Recorders:** The signal from the detection unit is received by the recorder and the absorption band is recorded.

Applications

1. **In qualitative analysis:** Organic compounds show characteristic absorption in UV–visible region. So the presence of a specific compound can be known by comparing its absorption band with the absorption band of known compounds available in reference books. For example, the presence of benzene can be confirmed if absorption band appears at 255 nm.
2. **In quantitative analysis:** The amount of solute in a solution or concentration of a solution can also be determined by UV–visible spectroscopy. The determination can be done on the basis of Beer–Lambert's law, that is, $\log I_0/I = \in Cx$, where, I_0 is intensity of incident radiation, I is intensity of transmitted radiation, $\in$ is molar extinction coefficient, C is concentration of the solution and x is the path length.

Concept Check

- What is vacuum UV region?
- Write notes on $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions.
- Differentiate between chromophore and auxochrome.
- What is bathochromic shift?

3.5 Infrared Spectroscopy

The interaction of IR radiation with matter to determine its structure and properties is called **IR spectroscopy**. It causes vibration of bonds in molecules. Hence, IR spectroscopy is also called **vibrational spectroscopy**. The IR region of the electromagnetic spectrum may be divided into three main sections. These are as follows:

1. Near IR (overtone region) 0.8–2.5 μ (12500–4000 cm^{-1})
2. Middle IR (vibration–rotation region) 2.5–50 μ (4000–200 cm^{-1})
3. Far IR (rotation region) 50–1000 μ (200–100 cm^{-1})

The main region of interest for analytical purpose is from 4000 to 400 cm^{-1}.

Source of infrared is Nernst glower which consists of a rod of sintered mixture of the oxides of zirconium, yttrium and erbium. The rod is electrically heated to 1500°C to produce infrared radiation.

Basic Principle

When infrared radiation is made incident on the sample, it causes vibration of bonds present in the molecules. In other words, infrared radiation brings about the changes in vibrational energy levels of the molecule. The energy or frequency of infrared radiation that causes bond vibration depends on strength of bond, masses of atoms and arrangement of atoms within the molecule. It means that greater the bond strength, higher is the frequency of infrared radiation required to cause bond vibration. The order of stretching frequency of different bonds is:

Triple bond > Double bond > Single bond

All molecules do not absorb infrared radiation. Absorption takes place in infrared region in accordance with the following two **selection rules**.

1. The necessary condition for a molecule to absorb infrared radiation is that there should be a change in the magnitude or direction of the dipole moment on stretching. This change creates an oscillating dipole moment which interacts with the electrical component of incident infrared radiation. As a result, absorption of infrared radiation takes place by the molecule. Hence, molecules possessing permanent dipole moment show infrared absorption. Examples of IR active and inactive molecules are as follows:
   - In homonuclear diatomic molecules such as hydrogen (H_2), nitrogen (N_2), oxygen (O_2), fluorine (F_2) etc., there is no change in dipole moment during stretching of bonds and such molecules do not show infrared absorption. Thus, these molecules are said to be **IR inactive molecules** and cannot be analyzed by IR spectroscopy.
   - Stretching of heterodiatomic molecules brings change in magnitude of dipole moment and hence these are called **IR active molecules**. Such molecules are hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen iodide (HI), carbon monoxide (CO), etc.
2. Absorption of infrared radiation takes place when there occurs changes in vibrational energy levels by ±1 unit ($\Delta v = \pm 1$) as shown in Figure 6. Since molecules exist in the ground vibrational energy level (v_0), most common transitions are from v_0 to v_1 ($v_0 \rightarrow v_1$).

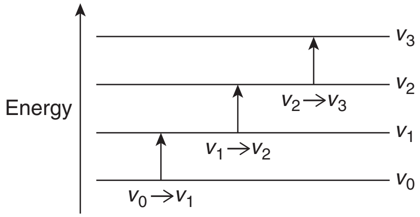


Figure 6 Vibrational energy levels showing different vibrational transitions.

Types of Bond Vibration

Vibration of bonds in a molecule may occur in two different ways. One is called **stretching vibration** and the other one is called **bending vibration**. These are shown in Figure 7.

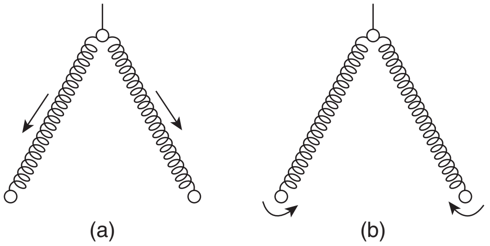


Figure 7 (a) Stretching vibration and (b) bending vibration.

1. **Stretching vibration:** In this type of vibration, the distance between two atoms increases or decreases but the atoms remain in the same bond axis. It is of two types:
   - **Symmetric stretching:** The movement of atoms with respect to a particular atom in a molecule occurs in the same direction for this kind of stretching vibration. It is shown in Figure 8(a).
   - **Asymmetric stretching:** In this case, one atom approaches to the central atom while the other departs from it as shown in Figure 8(b).

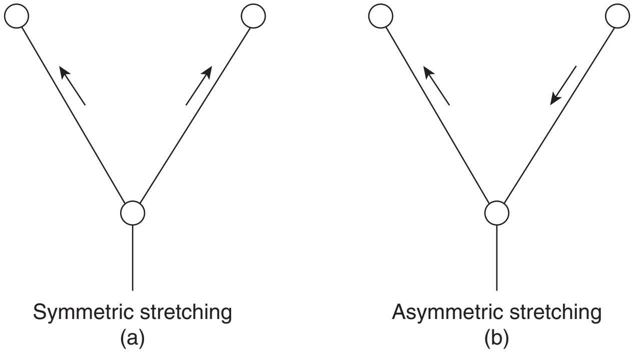


Figure 8 Different stretching vibrations.

2. **Bending vibration (Deformation):** The position of atoms changes with respect to the original bond axis in case of bending vibration. We know that more energy is required to stretch than that is required to bend. So, bending vibration occurs at low frequency as compared to stretching vibration. This vibration is of two types:
   - **Bending in plane:** In this case, the molecule undergoes bending vibration but all the three atoms remain in same plane. This can further be of two types:
     - **(a) Scissoring:** The two atoms approach each other or depart from one another in this type of bending vibration. It is shown in Figure 9(a).
     - **(b) Rocking:** In this case, movement of atoms takes place in the same direction as shown in Figure 9(b).

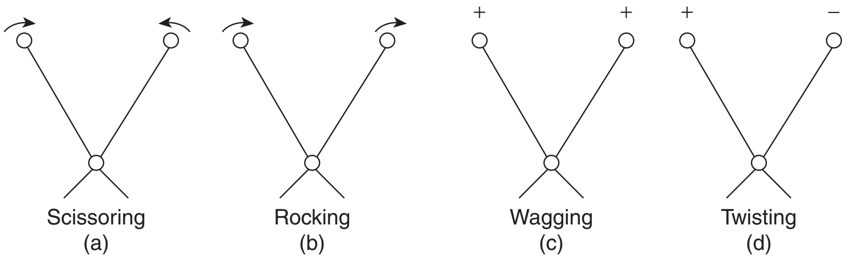


Figure 9 Different types of bending vibration. (+) sign shows that the atom is going above the plane of the molecule and (−) sign shows that the atom is going below the plane of the molecule.

- **Bending out of plane:** In this case, the atoms do not remain in the same plane. This is also of two types:
  - **(a) Wagging:** Two atoms in a molecule move above and below the plane with respect to the central atom in this type of bending vibration. This is shown in Figure 9(c).
  - **(b) Twisting:** In this case, one of the atoms moves above the plane while the other moves below with respect to the central atom as shown in Figure 9(d).

Bond Vibration in Diatomic Molecules

In case of simple diatomic molecules, we can calculate the vibrational frequencies by treating the molecule as a harmonic oscillator. The frequency of vibration is given by following relation.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ \mathrm{s}^{-1} \tag{3.15}$$

where ν is the frequency (vibrations per second), k is the force constant (It is defined as the stretching or restoring force between the two atoms in a molecule and is expressed in N/m.) and μ is the reduced mass per molecule (in kg). It is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{3.16}$$

where m_1 is the mass of one atom of the first element in a diatomic molecule (in kg) and m_2 is the mass of one atom of the second element in a diatomic molecule (in kg).

For example, let us consider a diatomic molecule AB where m_1 is the mass of one atom of A and m_2 is the mass of one atom of B. In spectroscopy, it is customary to quote absorption bands in units of wave number ($\bar{\nu}$). Wave number is expressed in cm^{-1}.
We know that $\bar{\nu} = \nu/c$ and $\lambda = c/\nu$. Putting the value of ν from Eq. (3.15), we get

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ \mathrm{cm}^{-1} \tag{3.17}$$

Problem 3

The fundamental vibrational frequency of HCl is 8.667 × 10^{13} s^{-1}. Calculate the force constant. Given that mass of ^{1}H is 1.008 g/mol and that of ^{35}Cl is 35.5 g/mol.

Solution

Given that $\nu = 8.667 \times 10^{13}\ s^{-1}$.
Mass of H = 1.008 g/mol.
Mass of Cl = 35.5 g/mol.

Mass of one atom of H (m_1) = $\frac{1.008}{6.023 \times 10^{23}}$ g

or $$m_1 = \frac{1.008}{6.023 \times 10^{23}} \times 10^{-3}\ \text{kg} = 1.673 \times 10^{-27}\ \text{kg}$$

Mass of one atom of Cl (m_2) = $\frac{35.5}{6.023 \times 10^{23}}$ g

or $$m_2 = \frac{35.5}{6.023 \times 10^{23}} \times 10^{-3}\ \text{kg} = 58.94 \times 10^{-27}\ \text{kg}$$

Reduced mass $$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.673 \times 10^{-27})(58.94 \times 10^{-27})}{(1.673 \times 10^{-27}) + (58.94 \times 10^{-27})}$$

or $$\mu = \frac{98.606 \times 10^{-54}}{60.613 \times 10^{-27}}$$
$$= 1.626 \times 10^{-27}\ \text{kg}$$

We know that $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

so, $$\nu^2 = \frac{1}{4\pi^2} \times \frac{k}{\mu}$$

or $$k = 4\pi^2 \nu^2 \mu$$

Putting the values of ν and μ, we get

$$k = 4\,(3.14)^2 \times (8.667 \times 10^{13})^2\,(1.626 \times 10^{-27})$$
$$= 481.7\ \text{kg/s}^2$$

Thus, force constant is found to be 481.7 kg/s^2.

Problem 4

The fundamental frequency of $^{12}C^{16}O$ molecule is 2170.2 cm^{-1}. Calculate the force constant of the given molecule. Given that the velocity of light c is 3×10^8 m/s.

Solution

Given that $\bar{\nu} = 2170.2\ cm^{-1} = 2170.2\ (10^{-2}\ m)^{-1} = 2170.2 \times 10^2\ m^{-1}$.

Mass of C = 12 g/mol.

Mass of O = 16 g/mol.

Mass of one atom of C $(m_1) = \dfrac{12}{6.023 \times 10^{23}}$ g

or $$m_1 = \frac{12}{6.023 \times 10^{23}} \times 10^{-3}\ \text{kg} = 1.992 \times 10^{-26}\ \text{kg}$$

Mass of one atom of O $(m_2) = \dfrac{16}{6.023 \times 10^{23}}$ g

or $$m_2 = \frac{12}{6.023 \times 10^{23}} \times 10^{-3}\ \text{kg} = 2.656 \times 10^{-26}\ \text{kg}$$

Reduced mass $\mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{(1.992 \times 10^{-26}) \times (2.656 \times 10^{-26})}{(1.992 \times 10^{-26}) + (2.656 \times 10^{-26})}$

or $$\mu = \frac{5.290 \times 10^{-52}}{4.648 \times 10^{-26}}$$
$$= 1.138 \times 10^{-26}$$

Again we know that $\bar{\nu} = \dfrac{1}{2\pi c}\sqrt{\dfrac{k}{\mu}}$

so, $$(\bar{\nu})^2 = \frac{1}{4\pi^2 c^2} \times \frac{k}{\mu}$$

or $$k = 4\pi^2 c^2 (\bar{\nu})^2\ \mu$$

Putting the values of $\bar{\nu}$ and μ, we get

$$k = 4\ (3.14)^2 \times (3 \times 10^8)^2\ (2170.2 \times 10^2)^2 (1.138 \times 10^{-26})$$
$$= 1902404406 \times 10^{-6}\ \text{kg/ s}^2$$
$$= 1902.404\ \text{kg/s}^2$$

Hence, the force constant of $^{12}C^{16}O$ is 1902.404 kg/s^2.

Number of Vibrations in Polyatomic Molecules

In a molecule with N atoms, each atom has three degrees of freedom along three coordinate axes. Hence there should be $3N$ degrees of freedom possible in that molecule. The translational movement uses three of $3N$ degrees of freedom. Similarly, rotation of non-linear molecule can be resolved into components about three perpendicular axes. So, a non-linear molecule is left with $3N-6$ degrees of freedom for internal vibrations. In case of linear molecules, there is no rotation about the bond axis, hence only two degrees of freedom are required, so there are $3N-5$degrees of freedom for vibrational motion.

Instrumentation

The instrument used in IR spectroscopy is called **infrared spectrophotometer**. The block diagram for infrared spectrophotometer is shown in Figure 10.

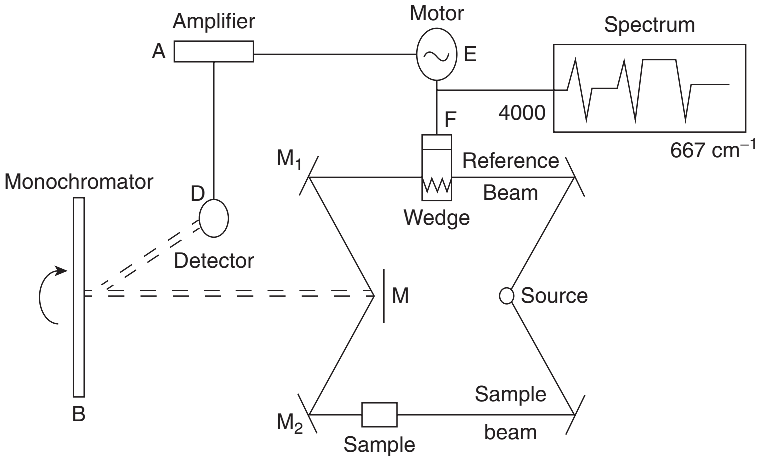


Figure 10 Block diagram for IR Spectrophotometer.

Different components of the spectrophotometer are described as follows:

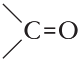
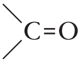
1. **Source:** It produces infrared radiations which are split into two beams. One of the beams is passed through the sample cell, which carries sample to be analyzed. This beam is called sample beam. The other beam is passed through the reference cell which carries reference. This beam is called reference beam.
2. **Sample and reference cell:** These are made up of sodium chloride or certain alkali metal halides because these are transparent to most of the IR region. Glass or quartz cannot be used for the manufacture of these cells as they absorb strongly in IR region.
3. **Chopper:** Both reference and sample beams are allowed to fall on a segmented mirror with the help of two mirrors M_1 and M_2. The segmented mirror is called chopper, which rotates at a definite speed and reflects sample and reference beam to the monochromator.
4. **Monochromator:** It sends frequencies from reference and sample beams separately to the detector.
5. **Detector:** It converts infrared radiation of a given frequency of sample or reference beam into electrical energy.
6. **Amplifier:** The electrical energy formed at the detector is amplified by an amplifier. Alternating current starts flowing from the detector to the amplifier because of the differences in the intensities of sample and reference beams.

7. **Wedge:** The amplifier is coupled to a small motor which drives the optical wedge. The movement of the wedge is in turn coupled to a pen recorder which draws absorption bands on the calibrated chart.

Applications

1. **Identification of compounds:** A particular group of atoms gives rise to characteristic absorption bands in IR spectrum. A few common groups, type of bond vibration and characteristic absorption frequencies are given in Table 2.

Table 2 Characteristic absorption bands of a few groups

Name of the Group	*Type of Bond Vibration*	*Absorption Frequency (cm^{-1})*
–OH	O–H stretching (non H-bonded)	~3700 (s)
–OH	O–H bonded (H-bonded)	3700 – 3300 (b)
–OH	O–H bending	1500 – 1200 (m, w)
–NH_2	N–H stretching	3300 – 3100 (s)
–NH_2	N–H bending	1700 – 1500
 (Saturated aldehydes)	C=O stretching	1740 – 1720 (s)
 (Saturated ketones)	C=O stretching	1725 – 1705(s)

Note: (s)- small, (b)- broad, (m)- medium, (w)- weak.

The characteristic absorption frequencies of different groups present in the unknown compound are obtained from IR spectrum of the compound and are matched with that of known compounds. From this, the unknown compound is identified. Some examples are described as follows:

- There should be 3 IR bands corresponding to symmetrical stretching (v_s or v_1), asymmetrical stretching (v_{as} or v_3) and symmetrical bending (δ or v_2) for sulphur dioxide (SO_2). The stretching vibrations are of higher energy than bending vibrations. Asymmetrical stretching is of higher energy than that of symmetrical stretching ($v_{as} > v_s > \delta$). In IR spectrum of SO_2, high intensity fundamental bands are observed at 1151 cm^{-1}, 519 cm^{-1} and 1361 cm^{-1} corresponding to v_1, v_2 and v_3 vibrations, respectively. Thus, an unknown compound showing bands at above fundamental frequencies can be identified as SO_2 molecule.
- In CO_2 molecule, there should be 4 vibrations possible. v_s does not bring about change in dipole moment and should be IR inactive. The IR active vibrations are asymmetrical stretching (v_{as}), symmetrical bending (δ) and outofplane bending (π). Though δ and π are different vibration modes, but for a linear molecule they are equivalent. So there occur two fundamental bands at 2349 cm^{-1} and 667 cm^{-1} corresponding to v_{as} and δ or π, respectively, in case of CO_2.

2. **Confirmation of presence of hydrogen bonding:** If intermolecular hydrogen bonding is present in a compound, the given bond between the two atoms in the molecule becomes weaker and absorption takes place at relatively less frequency (less wave number). For example, O–H stretching vibration occurs at ~3700 cm^{-1} for the molecules containing free –OH group (non-hydrogen bonded)

whereas that occurs below this range for the molecules containing hydrogen-bonded –OH group like water. Hence, presence of hydrogen bond in a compound can be identified from its IR spectrum. Figure 11 shows the infrared spectrum of methanol. A broad band appearing around 3300 cm^{-1} indicates stretching vibration of hydrogen-bonded –OH bond, which is due to the presence of intermolecular hydrogen bonding in between methanol molecules.

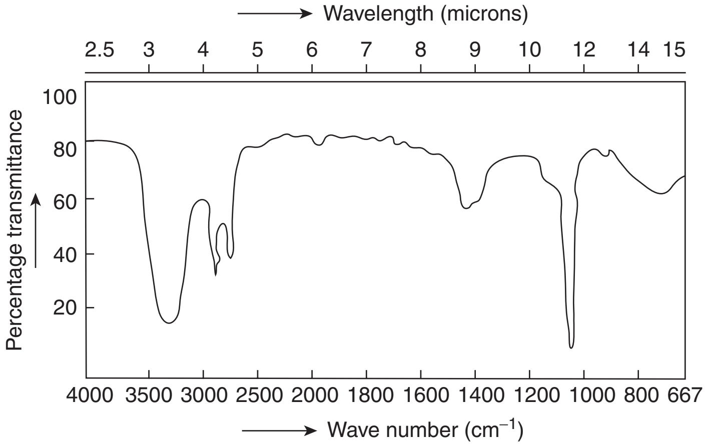
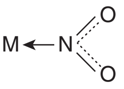


Figure 11 Infrared spectrum of methanol.

3. **Confirmation of coordination bond in compounds:** The coordination of the ligand atom with the metal ion in a coordination compound results in the movement of electron density from the ligand atom to the central metal ion. As a result, the bond between the two atoms in a ligand molecule becomes weaker and absorption of IR radiation occurs at relatively lower frequency. For example, coordination of nitrogen atom of –NH_2 group with metal ion in a coordination compound causes movement of electron density from N atom of N–H bond. This makes N–H bond weaker and hence the N–H stretching vibration occurs at lower frequency than that in free –NH_2 group (i.e., $v_s = 3100$ cm^{-1}).
4. **Identification of bonding site in complex compounds:** In some ligand species, there are more than one donor atoms which have ability to form coordination bonds with the central metal ion in a complex compound. Therefore, exact bonding site in a complex compound cannot be found out easily. However, it can be identified from IR spectra. For example, NO_2^- can be present in a complex compound in three forms.
   - Anionic nitrite ([M X_m]$(NO_2)_n$).
   - NO_2^- can coordinate to metal atom/ion through N-atom. Such complexes are called **nitro complexes**.
   - NO_2^- can also coordinate through one oxygen atom. These complexes are called **nitrito complexes**.



Nitro

$M \leftarrow O—N=O$

Nitrito

An anionic NO_2^- group shows three IR bands at 1335 cm^{-1} due to asymmetric stretching and at 1250 cm^{-1} due to symmetric stretching of N–O bond whereas the band at 850 cm^{-1} corresponds to in-plane bending vibration. In case of coordination of NO_2^- through N-atom, above three bands occur at relatively lower frequency due to polarization of N–O bond. On the other hand, if the coordination of NO_2^- is through O-atom, two stretching vibrations occur at 1468 cm^{-1} and 1065 cm^{-1} due to presence one N–O single bond and one N=O double bond. The bending vibration occurs at 825 cm^{-1}.

5. **Detection of impurities in a sample:** Impurities present in a sample will give extra absorption bands. By comparing IR spectra of pure compound, presence of impurities can be detected.

Concept Check

- What is the wavelength range for middle IR region?
- What is used as the source in IR spectrophotometer?
- Discuss the different types of bond vibrations.
- Why are glass or quartz cells not used in IR spectrophotometer?
- The wave number of the fundamental vibration of $^{79}Br - {}^{81}Br$ is 323.2 cm^{-1}. Calculate the force constant of the bond. (Mass of ^{79}Br = 78.9183 amu and ^{81}Br = 80.9163 amu).

3.6 Microwave Spectroscopy

Interaction of microwave radiation with matter to determine its structure and properties is called **microwave spectroscopy**. There occur changes in rotational energy levels of the molecules due to interaction of incident microwave radiation and hence it is called **rotational spectroscopy**. Microwave radiation of electromagnetic spectrum possesses wavelength range from 0.1 to 50 cm.

Basic Principle

When a molecule with permanent dipole moment rotates, a fluctuating or oscillating electric field is created. If the frequency of oscillation of the molecule becomes identical to frequency of electric field component of incident microwave radiation, then the phenomenon of resonance occurs. As a result of this, transfer of energy may take place by any one of the following two ways.

1. When there is a jump from lower rotational energy level to higher rotational energy level, transfer of energy takes place from incident microwave radiation to the molecule. In this case, the molecule exhibits absorption microwave spectrum.
2. When there is a jump from higher rotational energy level to lower rotational energy level, transfer of energy takes place from the molecule to incident microwave radiation. In such case, the molecule exhibits emission microwave spectrum.

The emission or absorption in microwave region takes place according to the following **selection rules**.

1. A rotating molecule must possess a permanent dipole moment so as to interact with oscillating electric field associated with microwave radiation. Thus a molecule with permanent dipole moment can interact with the electric field component of microwave radiation. Therefore, such a molecule exhibiting the rotational (or microwave) spectrum, is known as **microwave active** molecule. These molecules are HCl, HF, CO, etc. Molecules possessing zero dipole moment do not exhibit the rotational spectrum and such a molecule is known as **microwave inactive** molecule. These molecules are H_2, O_2, N_2 etc.

2. The rotating molecule can increase or decrease its rotational energy only to either next higher or next lower energy level, when it absorbs or emits a quantum of microwave radiation (i.e., $\Delta J = \pm 1$) as shown in Figure 12.

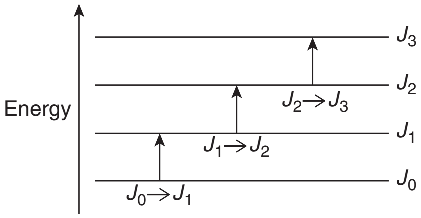


Figure 12 Rotational energy levels showing different rotational transitions.

Rotational energy levels are not quantized in solid and liquid states. So, changes in rotational energy levels in case of molecules existing in solid and liquid states do not occur. Consequently, solid and liquid molecules do not exhibit rotational spectra. In case of gaseous molecules, rotational energy levels are quantized and hence there occurs changes in rotational energy levels by absorption or emission of microwave radiation. As a result, microwave spectra or rotational spectra are observed only in case of molecules existing in gaseous state.

Microwave Spectra of Diatomic Molecules

Let us consider a diatomic molecule AB of equilibrium bond length r rotating about its axis through center of gravity (Figure 13). Let mass of A and B be m_1 and m_2, respectively. The distance between center of gravity and A is considered as r_1. Similarly, the distance between center of gravity and B is taken as r_2.

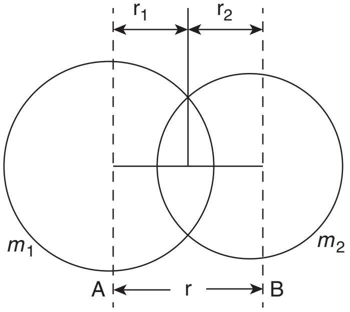


Figure 13 Diatomic molecule AB.

Evidently, the equilibrium bond length is $r = r_1 + r_2$. So,

$$r_2 = r - r_1 \tag{3.18}$$

The molecule rotates end-over-end about the center of gravity. This is defined by the balancing equation

$$m_1 r_1 = m_2 r_2$$

or $$m_1 r_1 = m_2 (r - r_1) = m_2 r - m_2 r_1 \Rightarrow m_1 r_1 + m_2 r_1 = m_2 r \Rightarrow r_1 (m_1 + m_2) = m_2 r$$

or $$r_1 = \frac{m_2 r}{m_1 + m_2} \tag{3.19}$$

Similarly,
$$r_2 = \frac{m_1 r}{m_1 + m_2} \tag{3.20}$$

Again, moment of inertia of the rotating molecule, $I = m_1 r_1^2 + m_2 r_2^2$. Substituting Eqs. (3.19) and (3.20), we get

$$I = m_1 \frac{m_2^2 r^2}{(m_1 + m_2)^2} + m_2 \frac{m_1^2 r^2}{(m_1 + m_2)^2} = \frac{m_1 m_2^2 r^2 + m_2 m_1^2 r^2}{(m_1 + m_2)^2} = \frac{m_1 m_2 r^2 (m_1 + m_2)}{(m_1 + m_2)^2} = \frac{m_1 m_2}{m_1 + m_2} r^2$$

or
$$I = \mu r^2 \tag{3.21}$$

where μ is reduced mass and can be given by $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

Angular momentum (L) of the rotating molecule can be given by

$$L = I\omega \tag{3.22}$$

where ω is angular velocity and I is moment of inertia.
But angular momentum is quantized and is given by

$$L = \frac{\mathrm{h}}{2\pi}\sqrt{J(J+1)} \tag{3.23}$$

where J is rotational quantum number and represents different rotational energy levels and h is Planck's constant.
Energy of rotating molecule is given by

$$E = \frac{1}{2} I\omega^2 \tag{3.24}$$

or
$$E = \frac{1}{2} \times \frac{(I\omega)^2}{I} \tag{3.25}$$

Putting the value of $I\omega$ from Eq. (3.22) in Eq. (3.25), we get

$$E = \frac{(L)^2}{2I} \tag{3.26}$$

Putting the value of L from Eq. (3.23) in Eq. (3.26), we get

$$E = \frac{1}{2I}\left[\frac{\mathrm{h}}{2\pi}\sqrt{J(J+1)}\right]^2$$

or
$$E = \frac{\mathrm{h}^2}{8\pi^2 I} J(J+1) \tag{3.27}$$

In spectroscopy, it is customary to report the energy (E) in terms of wave number (i.e., in terms of cm^{-1}).

$$E = \frac{\text{h}c}{\lambda} \Rightarrow \frac{1}{\lambda} = \frac{E}{\text{h}c} = E_J$$

where E_J is the rotational energy of J^{th} rotational energy level of the molecule expressed in cm^{-1}.

Thus,
$$E_J = \frac{\text{h}^2}{8\pi^2 I c \text{h}} J(J+1) = \frac{\text{h}}{8\pi^2 I c} J(J+1)$$

or
$$E_J = BJ(J+1) \tag{3.28}$$

where B is rotational constant ($B = \text{h}/8\pi^2 Ic$).

Equation (3.28) represents the expression for rotational energy of J^{th} rotational energy level of the rotating molecule. For example, energy of first rotational energy level ($J = 1$) can be given by

$$E_1 = B \times 1\ (1 + 1) = 2B.$$

Rotational energy (E_J) of corresponding rotational energy level (J) are shown in Figure 14.

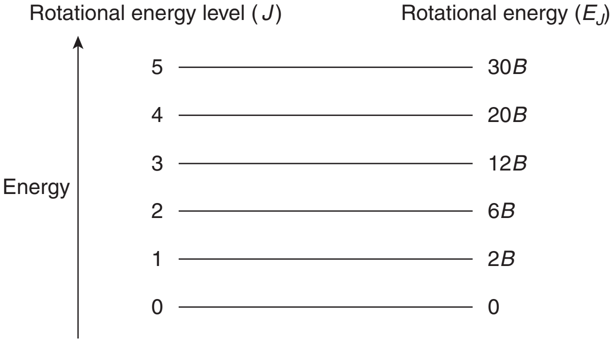


Figure 14 Various rotational energy levels and their corresponding energies.

From Figure 14, it can be seen that the energy gap between first energy level ($J = 1$) and ground energy level ($J = 0$) is $2B - 0 = 2B$. This energy gap is represented by $J_{0\rightarrow1}$ transition. In other words, $J_{0\rightarrow1}$ transition occurs by absorption of $2B$ amount of energy. Similarly, $J_{1\rightarrow2}$, $J_{2\rightarrow3}$, $J_{3\rightarrow4}$ and $J_{4\rightarrow5}$ transitions occur at $4B$, $6B$, $8B$ and $10B$, respectively. Each transition corresponds to a peak which is shown in Figure 15. The gap between any two consecutive peaks (transition) is $2B$. In other words, rotational transitions are equally spaced with a spacing of $2B$.

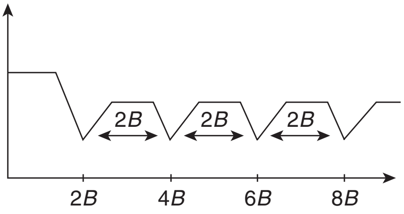


Figure 15 Peaks of microwave spectra of a molecule.

Instrumentation

The instrument used in microwave spectroscopy is called **microwave spectrophotometer**. The block diagram for infrared spectrophotometer is shown in Figure 16.

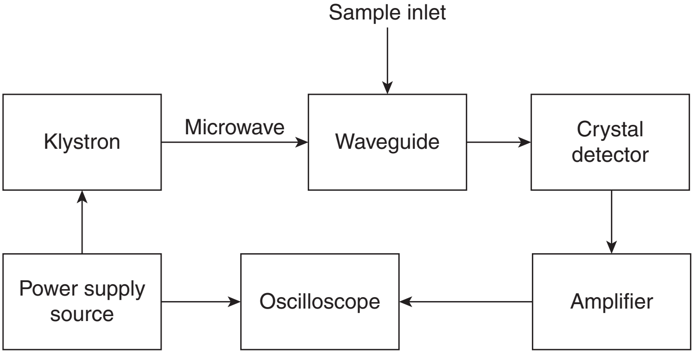


Figure 16 Block diagram for microwave spectrophotometer.

Different components of the spectrophotometer are discussed below:

1. **Klystron:** It is the source for generating microwave radiation.
2. **Waveguide:** It is a hollow metallic conductor in which microwave radiation can be transmitted from a Klystron (source) to the crystal detector.
3. **Crystal detector:** It utilizes piezoelectric crystal for the determination of frequency or wavelength of a radiation. Barium titanate, quartz, Rochelle salt, etc., are called piezoelectric crystals. When frequency of incident microwave radiation matches with the natural frequency of vibration of the crystal, an alternating electric field is created across the crystal.
4. **Amplifier and oscilloscope:** The electrical signal coming from the crystal is amplified by an amplifier and finally displayed as wave pattern on the screen of the oscilloscope.

Applications

1. **Determination of bond length of gaseous polar molecules:** Bond length of gaseous polar molecules can be determined by the following formula

$$r = \sqrt{\frac{I}{\mu}}$$

where μ is the reduced mass and I is the moment of inertia of the molecule.
Moment of inertia can be found out by the following relation

$$I = \frac{\mathrm{h}}{8\pi^2 Bc}$$

where h is the Planck's constant, c is the velocity of light and B is the rotational constant.
The value of B can be obtained from microwave spectrum of the molecule, and hence the bond length of the molecule can be determined.

2. **Determination of dipole moment of gaseous molecules:** Dipole moment of gaseous molecules can be determined by recording pure rotational spectra in the presence of a strong external field. When an electric field is applied to the sample being studied, the rotational lines of the molecule are split. The magnitude of splitting depends upon dipole moment (D) and strength of the applied electric field (E) as per following equation

$$\Delta \nu = (DE)^2 \tag{3.29}$$

where $\Delta \nu$ is the shift of rotational frequency by an external electrical field E.
The value of $\Delta \nu$ can be obtained from microwave spectrum of the molecule. Strength of applied electric field is known. Putting these values, dipole moment of the molecule can be determined.

Problem 5

A microwave spectrum of gaseous HCl molecule exhibits a series of equally spaced lines with interspacing of 20.7 cm^{-1}. Calculate the bond length of HCl molecule.

Solution

We know that the gap between any two consecutive microwave spectral lines is $2B$ and it is given that the microwave spectrum of gaseous HCl molecule gives equally spaced lines with interspacing of 20.7 cm^{-1}. So, $2B = 20.7$ cm^{-1} and therefore,

$$B = \frac{20.7}{2} = 10.35 \text{ cm}^{-1} = 10.35\ (10^{-2}\text{m})^{-1} = 1035 \text{ m}^{-1}$$

We know that,

Mass of H = 1.008 g/mol.
Mass of Cl = 35.5 g/mol.

So, mass of one atom of H $(m_1) = \dfrac{1.008}{6.023 \times 10^{23}}$ g

or $$m_1 = \frac{1.008}{6.023 \times 10^{23}} \times 10^{-3} \text{ kg} = 1.673 \times 10^{-27} \text{ kg}$$

Mass of one atom of Cl $(m_2) = \dfrac{35.5}{6.023 \times 10^{23}}$ g

or $$m_2 = \frac{35.5}{6.023 \times 10^{23}} \times 10^{-3} \text{ kg} = 58.94 \times 10^{-27} \text{ kg}$$

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.673 \times 10^{-27})(58.94 \times 10^{-27})}{(1.673 \times 10^{-27}) + (58.94 \times 10^{-27})}$$

or $$\mu = \frac{98.606 \times 10^{-54}}{60.613 \times 10^{-27}} = 1.626 \times 10^{-27} \text{ kg}$$

The value of I can be obtained from the following formula.

$$B = \frac{\mathrm{h}}{8\pi^2 Ic}$$

where h is the Planck's constant = 6.626×10^{-34}Js and c is the velocity of light = 3×10^8 m/s. So,

$$I = \frac{\mathrm{h}}{8\pi^2 Bc} = \frac{6.626 \times 10^{-34}}{8(3.14)^2 1035 \times 3 \times 10^8} = 2.705 \times 10^{-47}\ \mathrm{kg\ m^2}$$

Again we know that, $I = \mu r^2$

or $$r = \sqrt{\frac{I}{\mu}}$$

where I is the moment of inertia and μ is the reduced mass.

$$r = \sqrt{\frac{2.705 \times 10^{-47}}{1.626 \times 10^{-27}}}$$
$$= 1.289 \times 10^{-10}\ \mathrm{m} = 1.289\ \text{Å}$$

Hence, the bond length of HCl molecule is 1.289Å.

Problem 6

Calculate the energy of $J_{3 \to 2}$ *transition in the pure rotational spectrum of* $C^{12}O^{16}$*. The equilibrium bond length is 112.81pm.*

Solution

Energy of J^{th} rotational energy level can be given as

$$E_J = BJ(J + 1)$$

Similarly, energy of third rotational energy level, $E_3 = B_3(3 + 1)$

or $$E_3 = 12B$$

Energy of second rotational energy level, $E_2 = B_2(2 + 1)$

or $$E_2 = 6B$$

The amount of energy released for $J_{3 \to 2}$ transition, $\Delta E = E_3 – E_2$

or $$\Delta E = 12B - 6B = 6B$$

Again rotational constant B can be given by:

$$B = \frac{\mathrm{h}}{8\pi^2 Ic}$$

The value of moment of inertia (I) can be found as: $I = \mu r^2$.
Given that $r = 112.81\text{pm} = 112.81 \times 10^{-12}$ m:
We know that:
Mass of C = 12 g/mol.
Mass of O = 16 g/mol.

So, mass of one atom of C $(m_1) = \dfrac{12}{6.023\times10^{23}}$ g

or $$m_1 = \frac{12}{6.023\times10^{23}}\times10^{-3}\ \text{kg} = 1.992\times10^{-26}\ \text{kg}$$

Mass of one atom of O $(m_2) = \dfrac{16}{6.023\times10^{23}}$ g

or $$m_2 = \frac{16}{6.023\times10^{23}}\times10^{-3}\ \text{kg} = 2.656\times10^{-26}\ \text{kg}$$

Reduced mass $(\mu) = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{(1.992\times10^{-26})(2.656\times10^{-26})}{(1.992\times10^{-26})+(2.656\times10^{-26})}$

or $$\mu = \frac{5.290\times10^{-52}}{4.648\times10^{-26}} = 1.138\times10^{-26}\ \text{kg}$$

Putting the value of μ and r, the value of I is calculated as:

$$I = 1.138\times10^{-26}\times(112.81\times10^{-12})^2 = 1.448\times10^{-46}\ \text{kg m}^2$$

The value of rotational constant is

$$B = \frac{6.626\times10^{-34}}{8(3.14)^2\times1.448\times10^{-46}\times3\times10^8} = 19.34\ \text{cm}^{-1}$$

Now, $$\Delta E = 6B = 6\times19.34 = 116.04\ \text{cm}^{-1}$$

Thus, frequency of $J_{3\rightarrow2}$ transition in the pure rotational spectrum of $C^{12}O^{16}$ is found as 116.04 cm^{-1}.

Concept Check

- Why are rotational spectra of only gaseous molecules recorded?
- Discuss the basic principle of microwave spectroscopy.

- What is used as source in microwave spectrophotometer?
- Microwave spectrum of gaseous CN molecule exhibits a series of equally spaced lines with interspacing of 3.8 cm^{-1}. Calculate the internuclear distance of CN molecule.

Key Terms

Electromagnetic radiations
Beer–Lambert's law
Incident radiation
Transmitted radiation
Optical density
Transmittance
Absorbance
Molar extinction coefficient
UV–visible spectroscopy
Electronic energy levels
Electronic transitions
Sigma (σ) bonding molecular orbitals
Sigma (σ*) antibonding molecular orbitals
Pi (π) bonding molecular orbitals
Pi (π*) antibonding molecular orbitals
Non-bonding molecular orbitals
Instrumentation
Hydrogen discharge lamp
IR spectroscopy
Nernst glower
Selection rules
IR active molecules
IR inactive molecules
Dipole moment
Vibrational energy levels
Stretching bond vibration
Bending bond vibration
Fundamental frequency
Reduced mass
Force constant
Microwave spectroscopy
Resonance
Microwave absorption spectroscopy
Microwave emission spectroscopy
Rotational energy levels
Bond length or internuclear distance

Objective-Type Questions

Multiple-Choice Questions

1. The absorption of the far IR radiation causes a change in
   a. vibrational energy.
   b. rotational energy.
   c. electronic energy.
   d. both vibrational and rotational energy.
2. Which of the following molecules can show a pure rotational spectrum?
   a. CO_2
   b. H_2
   c. N_2
   d. HCl
3. The ratio of incident radiation to transmitted radiation is called
   a. absorbance.
   b. transmittance.
   c. opacity.
   d. none of these.
4. Which of the following electromagnetic radiations possesses shortest wavelength?
   a. Cosmic ray
   b. γ-ray
   c. Microwave
   d. Radio wave

5. Which of the following molecules exhibits only $\sigma \rightarrow \sigma^*$ transition?
   a. CO_2
   b. CH_4
   c. CH_3OH
   d. CH_3COCH_3

Fill in the Blanks

1. If a solution transmits 10% of the incident light, its optical density is _______.
2. The ratio of transmitted radiation to incident radiation is called _______.
3. The wavelength range for middle IR region is _______.
4. In microwave spectrum, the spectral lines are equally spaced with a gap of _______.
5. The energy required for $n \rightarrow \sigma^*$ transition is _______ than that required for $\pi \rightarrow \pi^*$ transition.

Review Questions

Short-Answer Questions

1. Arrange the following electromagnetic radiations in decreasing order of their energy: UV, visible, IR, X-ray and microwave.
2. What is molar extinction coefficient?
3. What is the unit of molar extinction coefficient?
4. What is the difference between atomic spectra and molecular spectra?
5. What are the possible electronic transitions in a molecule?
6. Arrange different electronic transitions in order of increasing energy.
7. Which types of electrons are involved in bond formation?
8. What are the selection rules for infrared spectroscopy?
9. Why does HBr show pure rotational spectrum whereas Br_2 does not?
10. Arrange the following in decreasing order. $\Delta E_{\text{vibrational}}$, $\Delta E_{\text{electronic}}$, $\Delta E_{\text{rotational}}$
11. What is force constant? Give its unit.
12. Why does methane not absorb IR radiation?
13. What are the limitations of microwave spectra?
14. Differentiate between microwave absorption spectroscopy and microwave emission spectroscopy.
15. Which type of bond vibration requires more energy: stretching or bending?

Long-Answer Questions

1. What is electromagnetic radiation? Discuss its characteristics.
2. State and explain Beer–Lambert's law.
3. Discuss various types of electronic transitions that occur in a molecule upon absorption of UV–visible radiation.
4. Draw the block diagram for UV–visible spectrophotometer and explain its different components.

5. Write the basic principle of IR spectroscopy. Discuss its important applications.
6. Draw the block diagram for IR spectrophotometer and explain its different components.
7. Discuss two important applications of microwave spectroscopy.
8. Draw the block diagram for microwave spectrophotometer and explain its different components.

Numerical Problems

1. The transmittance of an aqueous solution is 0.25 at 25°C for a 3.5×10^{-4} M solution in a 2 cm cell. Calculate the molar extinction coefficient.
2. In a certain cell, 0.001 M solution of a substance transmits 80% of the incident light. Find the concentration of a solution which will absorb 80% of the light when placed in the same cell.
3. A solution of thickness 2.0 cm transmits 40% of incident light. What is the concentration of the solution if the molar absorption coefficient is 8200 dm^3/mol/cm?
4. Determine the rotational energy of CO on the quantum level $J = 2$ if the bond distance of CO is 1.131 Å. Given that atomic masses of C and O are 12 g/mol and 16 g/mol, respectively.
5. The wave number of the fundamental vibration of $^{35}Cl_2$ is 564.9 cm^{-1}. Calculate the force constant of the bond.
6. In the microwave spectra of HBr, a series of lines having separation of 16.94 cm^{-1} are obtained. Calculate the internuclear distance of HBr. (Atomic mass of Br = 79.92 amu).

Answers

Multiple-Choice Questions

1. (b)
2. (d)
3. (c)
4. (a)
5. (b)

Fill in the Blanks

1. 1
2. transmittance
3. 2.5–50 μ
4. $2B$
5. greater

Numerical Problems

1. 8.6×10^2 L/mol/cm
2. 7.215×10^{-3} M
3. 2.426×10^{-5}mol/L
4. 116.04 cm^{-1}
5. 329.041 kg/s
6. 1.414 Å

4 Coordination Chemistry

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Central metal atom/ion, donor atoms, coordination number and ligands in a coordination compound.
- Various types of ligands.
- Guidelines for naming coordination complexes.
- Factors influencing the formation and stability of coordination complexes.
- Various theories explaining bond formation in coordination complexes.
- Effective atomic number, primary and secondary valencies of central metal atom/ion.
- Relation between coordination number and geometry of coordination compounds.
- Formation of octahedral and tetrahedral complexes.
- Magnetic properties and origin of color in transition metal complexes.

Coordination chemistry is the branch of chemistry which deals with the study of structure, magnetic and spectral properties of special class of compounds called *coordination compounds* or simply *complex compounds*. These compounds are prepared from the combination of more than one stable chemical species like the way double salts are prepared. But their properties are completely different from those of double salts. So it is required to know about double salts before discussing complex compounds in detail.

Double salts: When a mixture containing aqueous solutions of $FeSO_4$ and $(NH_4)_2SO_4$ are evaporated, crystals of Mohr's salt are obtained with molecular formula $\{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O\}$. Its crystal structure is completely different from that of its constituents ($FeSO_4$ and $(NH_4)_2SO_4$). In water, it dissociates to form Fe^{2+}, NH_4^+ and SO_4^{2-} ions. Such a compound is called a **double salt**. Thus double salts are compounds that are prepared by the combination of two or more stable chemical species and exist only in crystal lattices but break down into their constituent compounds when dissolved in water or in any other solvents. Their physical and chemical properties are same as that of their constituents. Some examples of double salts are as follows:

- Potash alum: $\{Al_2(SO_4)_3\ K_2\ SO_4 \cdot 24H_2O\}$
- Carnallite: $KCl \cdot MgCl_2 \cdot 6H_2O$

Coordination Compounds: When an aqueous solution of ammonia is added to aqueous solution of $NiCl_2$, the green colored solution of $NiCl_2$ changes to purple, due to formation of a compound corresponding to the formula $\{Ni(NH_3)_6\}Cl_2$.

$$\underset{\text{(Green)}}{NiCl_2(aq)} + 6NH_3 \rightarrow \underset{\text{(Purple)}}{[Ni(NH_3)_6]Cl_2}$$

Ni^{2+} ions completely disappear from the solution with the formation of new ions of composition $\{Ni(NH_3)_6\}^{2+}$. The solution on evaporation yields purple crystals. If these crystals are dissolved in water, they split into two kinds of ions as shown in the following reaction.

$$[Ni(NH_3)_6]Cl_2 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 2Cl^-$$

$[Ni(NH_3)_6]^{2+}$ion so formed does not give the test for Ni^{2+} and NH_3. This gives direct evidence for absence of free Ni^{2+} ions and NH_3 molecules in the solution. Hence, the compound has its own existence both in solid or in dissolved state and its properties are completely different from that of its constituents (i.e., $NiCl_2$ and NH_3). Such a compound is called **coordination** or **complex compound** and $[Ni(NH_3)_6]^{2+}$ is called a **complex** ion.

Thus coordination compound may be defined as a compound that results from the combination of two or more stable chemical species and retains its identity in the solid as well as in dissolved state *or* a compound which retains its identity even when dissolved in water or in any other solvent and its properties are completely different from those of its constituents. Some examples of coordination compounds are as follows:

- Hexammine Cobalt(III) chloride: $[Co(NH_3)_6]\ Cl_3$
- Potassium hexacyanoferrate(III): $K_3\ [Fe(CN)_6]$

Usually, transition metals form coordination compounds because of their small size, high nuclear charge and vacant orbitals in *d*-subshell of the penultimate shell (i.e., the shell which is situated just before the outermost shell).

4.1 Terms and Terminology in Coordination Chemistry

1. **Coordination sphere:** It consists of a central metal atom or ion and ligands. Coordination sphere is indicated by writing the symbol or formula of central metal atom/ion and ligands inside a square bracket, while writing the formula of a complex compound. For example, $[A(X)_n]B$ is a complex compound in which coordination sphere contains central metal ion A and ligand X.
2. **Central metal atom or ion:** The metal atom or ion that is present in coordination sphere is called central metal atom or ion. For example, Ni^{2+} ion is the central metal ion in the complex $[Ni(NH_3)_6]Cl_2$.
3. **Ligand:** A ligand is a species which can donate at least a pair of electrons to the central metal atom or ion to form coordinate bond with it. For example NH_3 acts as a ligand in the complex compound $[Ni(NH_3)_6]Cl_2$.
4. **Donor atom:** The atom in the ligand species, which donates electron pair to the central metal ion or atom is called donor atom.For example, in NH_3, N is the donor atom.
5. **Coordination number:** The ligands are attached to central metal atom or ion through coordinate bonds in complexes. *The total number of coordinate bonds formed between ligands and central metal atom or ion in a complex is called coordination number*. For example, coordination number of Ni^{2+} is 6 in $[Ni(NH_3)_6]Cl_2$ because six ammonia molecules form six coordinate bonds with Ni^{2+} in this complex. Similarly, coordination number of Co^{3+} in $[Co(en)_3]^{3+}$ is also six because three molecules of ethylenediammine form six coordinate bonds with Co^{3+} ion.
6. **Charge on a complex ion:** The charge carried by a complex ion is the algebraic sum of charges carried by central metal atom or ion and that by total number of ligand species coordinated to it. For example, the charge on $[Fe(CN)_6]^{4-}$ ion is –4. It is because one Fe^{2+} ion has a charge of magnitude +2 and six CN^- ions carry charge of magnitude –6.

   Based on the charge on a complex ion, complex compounds are classified into three categories.

   - **Cationic complex:** The complex compound is called cationic complex if the charge on its complex ion is positive. For example, $[Ni(NH_3)_6]Cl_2$ is a cationic complex because the complex ion $[Ni(NH_3)_6]^{2+}$ carries positive charge.

- **Anionic complex:** The complex compound is called anionic complex if the charge on its complex ion is negative. For example, $K_3[Fe(CN)_6]$ is an anionic complex because its complex ion $[Fe(CN)_6]^{3-}$ carries negative charge.
- **Neutral complex:** The complex compound is called neutral if it does not carry any charge on it. For example, $[Ni(CO)_4]$ is a neutral complex.

7. **Counter ion:** The ion which is present outside of the coordination sphere in a complex compound is called counter ion. For example, Cl^- is the counter ion in $[Ni(NH_3)_6]Cl_2$.

Classification of Ligands

Ligands are classified based on the type of charge on them and the number of electron pairs donated to central metal ion or atom.

Classification of Ligands based on the Type of Charge

Ligands can be classified into three categories depending on the charge on them.

1. **Anionic or negative ligands:** Ligand species containing negative charge on them are called *anionic* or *negative* ligands. For example, Cl^-, OH^-, NO_2^-, CN^-, etc.
2. **Neutral ligands:** Ligand species containing zero charge on them are called *neutral* ligands. For example, CO, H_2O, NH_3, etc.
3. **Cationic or positive ligands:** Ligand species containing positive charge on them are called *cationic* or *positive* ligands. NO^+, NO_2^+, etc.

Classification of Ligands based on the Number of Electron Pairs donated to Central Metal Ion or Atom

Ligands can also be classified into three categories depending on the number of electron pairs donated to the central metal ion or atom. The number of times a ligand bonds to the central metal ion or atom through non-contiguous donor sites is called its **denticity**.

1. **Unidentate or monodentate ligand:** Ligand which donates only one pair of electrons to central metal ion or atom is called *unidentate* or *monodentate* ligand. For example, NH_3, H_2O, Cl^-, Br^-, I^-, CN^-, OH^-, CO, NO_2^-, etc.
2. **Bidentate ligand:** Ligand which donates two pairs of electrons to the central metal ion or atom is called *bidentate ligand*. For example, oxalate ion $(C_2O_4^{2-})$, ethylenediamine ($H_2N–CH_2–CH_2–NH_2$)
3. **Polydentate ligand:** Ligand which donates more than two pairs of electrons to the central metal ion or atom is called *polydentate ligand*. For example, ethylenediamine tetraacetic acid (EDTA). It is a hexadentate ligand.

Some common ligands with their commonly abbreviated names and denticity are listed in Table 1.

Table 1 Some common ligands with their commonly abbreviated names and denticity

Ligand	*Formula*	*Most Common Denticity*
1,10-Phenanthroline (*phen*)	$C_{12}H_8\mathbf{N}_2$	Bidentate
2,2′-Bipyridine (*bipy*)	$(C_5H_4\mathbf{N})_2$	Bidentate

(*Continued*)

Table 1 Continued

Ligand	*Formula*	*Most Common Denticity*
Acetonitrile	CH_3CN	Monodentate
Acetylacetonate (*acac*)	$CH_3-C(\mathbf{O})-CH-C(\mathbf{O})-CH_3$	Bidentate
Alkenes	$R_2\mathbf{C}=\mathbf{C}R_2$	Bidentate
Ammonia (*ammine* or less commonly *amino*)	$\mathbf{N}H_3$	Monodentate
Azide (*azido*)	N_3^-	Monodentate
Bromide (*bromido*)	$\mathbf{Br}^-$	Monodentate
Carbon monoxide (*carbonyl*)	$\mathbf{CO}$	Monodentate
Chloride (*chlorido*)	$\mathbf{Cl}^-$	Monodentate
Cyanide (*cyanido*)	$\mathbf{CN}^-$	Monodentate
Cyclopentadienyl	$\{C_5H_5\}^-$	Monodentate
Diethylenetriamine (*dien*)	$C_4H_{13}N_3$	Tridentate
Dimethylglyoximate (*dmgH*$^-$)	$CH_3C(\mathbf{N}O^-)C(\mathbf{N}O^-)CH_3$	Bidentate
Ethylenediamine (*en*)	$\mathbf{N}H_2CH_2CH_2\mathbf{N}H_2$	Bidentate
Ethylenediaminetetraacetic acid (*EDTA*)	$(H\mathbf{OO}CH_2C)_2\mathbf{N}-CH_2-CH_2-$ $\mathbf{N}(CH_2C\mathbf{OO}H)_2$	Hexadentate
Ethylenediaminetriacetate	$(^-\mathbf{OO}CH_2C)_2\mathbf{N}-H_2C-CH_2-$ $\mathbf{N}H(CH_2C\mathbf{OO}^-)$	Hexadentate
Fluoride (*fluorido*)	$\mathbf{F}^-$	Monodentate
Glycinate	$H_2\mathbf{N}-CH_2-C\mathbf{OO}^-$	Bidentate
Hydroxide (*hydroxido*)	$\mathbf{O}-H^-$	Monodentate
Iodide (*iodido*)	$\mathbf{I}^-$	Monodentate
Isothiocyanate (*isothiocyanato*)	$\mathbf{N}=C=S^-$	Monodentate
Nitrate (*nitrato*)	$\mathbf{N}O_3^-$	Monodentate
Nitrite (*nitrito-O*)	$\mathbf{O}NO^-$	Monodentate
Nitrite (*nitrito-N*)	$\mathbf{N}O_2^-$	Monodentate
Oxalate (*oxalato*)	$[\mathbf{O}-C(=O)-C(=O)-\mathbf{O}]^{2-}$	Bidentate
Pyridine (*pyridino*)	$C_5H_5\mathbf{N}$	Monodentate
Sulphide (*thio* or less commonly bridging *thiolate*)	$\mathbf{S}^{2-}$	Monodentate (M=S) or bidentate bridging (M–S–M′)
Thiocyanate (*thiocyanato*)	$\mathbf{S}-CN^-$	Monodentate
Triethylenetetramine (*trien*)	$[CH_2\mathbf{N}HCH_2CH_2\mathbf{N}H_2]_2$	Tetradentate

(*Continued*)

Table 1 Continued

Ligand	*Formula*	*Most Common Denticity*
Trimethylphosphine	$\mathbf{P}Me_3$	Monodentate
Triphenylphosphine	$\mathbf{P}Ph_3$	Monodentate
Tris(2-aminoethyl)amine (*tren*)	$(NH_2CH_2CH_2)_3N$	Tetradentate
Tris(2-(diphenylphosphino)ethyl)amine (*np*$_3$)	$H_2\mathbf{N}CH_2–C(\mathbf{P}\mathbf{Ph_2})_3$	Tetradentate
Water (*aqua*)	H–**O**–H	Monodentate

Note: Commonly abbreviated names are written in italics within bracket. Bonding atoms shown in bold.

Concept Check

- Write the formula of any two bidentate and monodentate ligands.
- Identify central metal ion, ligand and find oxidation state of the central metal ion in $[Fe(CN)_6]^{4-}$.
- Find out the oxidation state and coordination number of the central metal atom in $[Ni(CO)_4]$.

4.2 Rules for Writing Formula of a Complex Compound

The formula of a complex compound is written according to following rules.

1. The symbol of the central metal atom or ion is written first. Symbol or formula of anionic ligands are then listed which are followed by that of neutral ligands. Symbols or formulae of cationic ligands are written next. These are then enclosed in a square bracket. For example, formula of triamminetrichlorocobalt(III)chloride is written as: $[CoCl_3(NH_3)_3]Cl_3$. In this case anionic ligand is Cl^-, which is written just after the symbol of central metal ion Co^{3+}. Then the formula of neutral ligand NH_3 is written.
2. If the complex compound contains more than one anionic ligand, the formulae are listed in alphabetical order according to the first symbol of their formula (and not their names). An exactly similar procedure is followed if there are more than one neutral ligand or cationic ligand present. For example, formula of triamminebromochloroiodocobalt(III) is $[Co\ BrClI(NH_3)_3]$. In this case, there are three anionic ligands, that is, Br^-, Cl^- and I^-. Since Br^- comes first alphabetically, its symbol is written just after the symbol of central metal ion Co^{3+}. Similarly, the symbols of other two anionic ligands are written.
3. The polyatomic ligands are written in parentheses.
4. The complicated organic ligands may be listed in the formula with their commonly accepted abbreviated names in parentheses. For example, the formula of ethylenediamine can be written by its commonly abbreviated name "en". Their place in the formula is decided by the first symbol of their formulae and not by the first letter of their common names.
5. There should be no space between the cationic and anionic species while writing the formula.

4.3 Nomenclature of Coordination Compounds

Following rules are recommended by International Union of Pure and Applied Chemistry (IUPAC) for the nomenclature of coordination compounds.

1. In case of cationic or anionic complex compounds, the cationic part is named first and then the anion. The neutral complex compound is given one word name. For example, cationic part of $[Ni(NH_3)_6]Cl_2$ is $[Ni(NH_3)_6]^{2+}$, which is named first, then the name of Cl^- is written.
2. Ligands are named first followed by central metal atom or ion, while naming the coordination sphere in a complex compound. In case of $[Ni(NH_3)_6]^{2+}$, name of ammonia is written first and then the name of Ni^{2+} is written.
3. Name of cationic ligand ends with "ium" and that of anionic ligand ends with letter "o". Anionic ligand having name ending with "ate" is written as "ato" (nitrate → nitrato); anionic ligands with name ending with "ite" is written as "ito" (nitrite → nitrito) and anionic ligands having name ending with "ide" is written as "ido" (fluoride → fluorido). Ambidentate ligands are named by indicating the bonding site, for example, cyanido ($\leftarrow C\bar{N}$) and isocyanido ($\leftarrow N\bar{C}$). The neutral ligand is named with specific name. IUPAC names of some common ligands are given in Table 2.

Table 2 IUPAC names of some common ligands

Name of Ligand	*Symbol/Formula*	*Kind*	*IUPAC Names*
Fluoride	F^-	Anionic	fluorido
Chloride	Cl^-	Anionic	chlorido
Bromide	Br^-	Anionic	bromido
Iodide	I^-	Anionic	iodido
Cyanide	CN^-	Anionic	cyanido
Acetate	CH_3COO^-	Anionic	acetato
Hydroxide	OH^-	Anionic	hydroxido
Oxalate	$C_2O_4^{2-}$	Anionic	oxalato
Peroxide	O_2^{2-}	Anionic	peroxo
Hydride	H^-	Anionic	hydrido
Nitrite	NO_2^-	Anionic	nitrito-N or dioxonitrato-N
	ONO^-	Anionic	nitrito-O or dioxonitrato-O
Nitrate	NO_3^-	Anionic	nitrato or trioxonitrato
Sulphate	SO_4^{2-}	Anionic	sulphato or tetraoxosulphato
Carbonate	CO_3^{2-}	Anionic	carbonato or trioxocarbonato
Amide	NH_2^{2-}	Anionic	amido
	NH^{2-}	Anionic	imido
Thiocyanate	SCN^-	Anionic	thiocyanato-S
Isothiocyanate	NCS^-	Anionic	thiocyanato-N

(*Continued*)

Table 2 (Continued)

Name of Ligand	*Symbol/Formula*	*Kind*	*IUPAC Names*
Nitronium	NO_2^+	Cationic	nitronium
Nitrosonium	NO^+	Cationic	nitrosonium
Water	H_2O	Neutral	aqua
Ammonia	NH_3	Neutral	ammine
Nitric oxide	NO	Neutral	nitrosyl
Carbon monoxide	CO	Neutral	carbonyl

4. The number of ligand species attached to the central metal atom or ion is indicated by writing suitable numerical prefixes such as *di*-, *tri*-, *tetra*-, etc. before their names. If the same ligand species are present twice, numerical prefix *di*- is used. Similarly, if the same ligand species is present three, four, five, six, etc. number of times, numerical prefixes *tri*-, *tetra*-, *penta*-, *hexa*-, etc. are used, respectively. For example, hexaammine is written if six ammonia molecules are present as ligands in a complex.
5. There are some ligands which contain *di*-, *tri*-, etc. in their names. In such cases, the number of ligand species is indicated by writing numerical prefixes such as *bis*- (for two number of species), *tris*- (for three number of species), *tetrakis*- (for four number of species), etc. before the names of these ligands. Names of these ligands are written in parentheses in such cases. Suppose three molecules of triphenylphosphine are present in a complex compound, its name is written as *tris*(triphenylphosphine) instead of *tri*(triphenylphosphine) since the name itself contains *tri*-.

   In case, use of affixes such as *di*-, *tri*-, etc. before the names of some ligands creates ambiguity, the number of such ligands are indicated by the numerical prefixes such as *bis*-, *tris*-, etc. The names of these ligands are written in parentheses. For example, the name of two molecules of methylamine is written as *bis*(methylamine) in a complex compound instead of dimethylamine in order to avoid confusion. It is because the word 'dimethyl' gives different meaning.
6. The ligands are named according to alphabetical order irrespective of their kind. If a complex contains more than one kind of ligand, their names are written according to alphabetical order. Suppose a complex compound contains a neutral ligand ammonia and an anionic ligand chloride ion, the name of ammonia is first written followed by that of chloride ion since ammonia comes first alphabetically.
7. When the coordination compound is anionic, the name of the central metal ion ends in -*ate*. For cationic and neutral complexes, the name of central metal ion or atom is given without any characteristic ending. For anionic complexes, the Latin names of metals are commonly used. A few metals and their Latin names with characteristic ending are given in Table 3.

Table 3 Latin names of a few metals

Name of the Metal	*Symbol*	*Latin Name*
Copper	Cu	Cuprate
Iron	Fe	Ferrate
Silver	Ag	Argentate
Tin	Sn	Stannate
Gold	Au	Aurate

8. The oxidation state of the central atom or ion is designated by a Roman numeral in parentheses just after its name without a space between the two. For example, oxidation state of central metal ion in $[Ni(NH_3)_6]Cl_2$ is +2. It is written as (II). Thus, the IUPAC name of the above complex compound is hexaamminenickel(II)chloride. The IUPAC names of a few complex compounds are listed as follows:
   - $[Co(NH_3)_6]Cl_3$ Hexaamminecobalt (III) chloride
   - $[Fe(H_2O)_6]SO_4$ Hexaaquairon(II) sulphate
   - $[PtCl_2(NH_3)_4]Br_2$ Tetraamminedichloroplatinum(IV) bromide
   - $K_3[Fe(CN)_6]$ Potassium hexacyanoferrate(III)
   - $[Ni(CO)_4]$ Tetracarbonylnickel(0)
   - $[Co(en)_3]_2(SO_4)_3$ tris (ethylenediammine) cobalt(III)sulphate
   - $K[BF_4]$ Potassiumtetrafluoro borate(III)

Concept Check

- Write the IUPAC names of $[Cr(NH_3)_3(H_2O)_3]Cl_3$ and $(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$.
- Write the formulae of chloronitroammineplatinum(IV) sulphate and diammine *bis*(ethylenediammine)cobalt(III) chloride.

4.4 Stability of Complex Ions

Usually the complex ions are highly stable. However, they dissociate to a small extent in an aqueous solution. Let us consider the dissociation of a complex ion $[Ag(NH_3)_2]^+$ in its aqueous solution.

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

The dissociation constant K can be given by:

$$K = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+} \tag{4.1}$$

It has been found that the dissociation constant of this complex ion is 6×10^{-8}, which is very small. It means the degree of dissociation of the complex ion is extremely small or the complex ion is dissociated to a small extent. In other words, the complex ion is highly stable. It can thus be said that smaller the value of dissociation constant, greater is the stability of the complex ion. Therefore, stability constant of the complex ion is the reciprocal of dissociation constant.

$$\frac{1}{K'} = K$$

where K' is the stability constant of this complex ion.

So,
$$K' = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \tag{4.2}$$

Greater the value of stability constant, higher will be the stability of the complex ion. Stability constant of the above complex ion $K' = 1/(6 \times 10^{-8}) = 1.67 \times 10^7$ which is a very high value. Thus, this complex ion is highly stable.

Let us consider the formation of the complex ion as shown below.

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

The equilibrium constant of this reaction is given by

$$K'' = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \tag{4.3}$$

Comparing Eqs. (4.2) and (4.3), we get K′ = K″. Thus the stability constant of the complex ion $[Ag(NH_3)_2]^+$ is the equilibrium constant of its formation.

Factors Affecting the Stability of a Complex Ion

The stability of complex ions depends on the nature of the central metal ion and the nature of the ligands present in it.

1. **Nature of central metal ion:** Following properties of a central metal ion in a complex are responsible for the stability of a complex ion.
   - **Charge density:** The ratio of charge on the central metal ion to its radius (size) is called its *charge density*. If a central metal ion possesses high magnitude of charge and smaller size, its charge density would be larger. Greater the charge density on the central metal ion, greater is the stability of its complexes. It is because central metal ion with high charge density (+ve) attracts the ligands (–ve) strongly forming a more stable complex. For example, Fe^{3+} ion has high charge density due to greater magnitude of charge on it and its smaller size than that of Fe^{2+}. Hence the complexes of Fe^{3+} are more stable than that of Fe^{2+}.

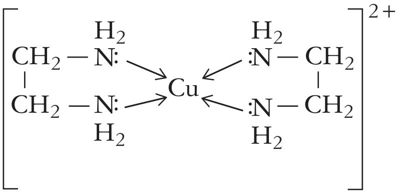
     Charge density of central metal ion increases when its size is decreased by keeping the magnitude of charge constant. For example, ionic radii decrease from $Mn^{2+}$to Cu^{2+}as shown below.

Central metal ion:	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Ionic radii (Å):	0.91	0.83	0.82	0.78	0.69
Stability of complexes:			$\xrightarrow[\text{Increases}]{}$		

     This causes increase in charge density from $Mn^{2+}$to Cu^{2+}. Thus, stability of complexes of Mn^{2+} is minimum where as that of Cu^{2+} is maximum among the above metal ions.
   - **Electronegativity:** Central metal ion with high electronegativity attracts the ligands strongly. This makes metal – ligand bond strong. As a result a stable complex is formed. So, greater the electronegativity of the central metal ion, higher is the stability of its complex.
2. **Nature of ligand**: Following properties of a ligand in a complex are responsible for the stability of a complex ion.
   - **Charge density:** Greater the charge density on the ligand, more stable is the complex formed. Thus, F^- ion with high charge density forms more stable complexes than those formed by Cl^- ions with lower charge density.
   - **Basic nature:** Basic ligands are strongly attracted by the positively charged central metal ion in a complex. As a result, these ligands donate their electron pair to the vacant *d*-orbitals of the central metal ion easily. This causes the formation of strong bonding between the two, due to which highly stable complexes are formed. Therefore, strongly basic ligands such as CN^-, F^-, NH_3, etc., form highly stable complexes. For example, $[CoF_3(NH_3)_3]$ is more stable than $[CoCl_3(NH_3)_3]$ because of presence of strongly basic ligand F^- ions in former case.

Chelate effect

Ligands having more than one donor site form coordinate bonds with the central metal atom or ion in such a way that the complex is formed with a closed ring structure. This resulting complex is called a **chelate** and those ligands, which form it are called **chelating ligands**. Usually, bidentate or polydentate ligands form chelates and hence these are called chelating ligands. For example, ethylenediamine (en) is a bidentate ligand which forms coordinate bonds with Cu^{2+} ion to form chelate ion as shown below.



Chelate cation

The complexes containing chelate rings are known to be more stable than those containing simple (unidentate) ligands. This effect is known as **chelate effect**. The greater stability of chelates can be explained on the basis of two factors which are discussed as follows:

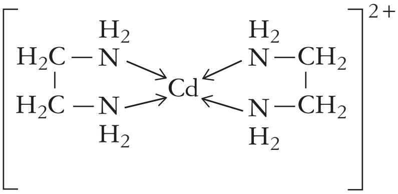
1. Let us consider the formation of complexes from hydrated cadmium ion $[Cd(H_2O)_4]^{2+}$ with methylamine (CH_3NH_2) and ethylenediamine (en).

$$[Cd(H_2O)_4]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+} + 4H_2O \quad (4.4)$$

The stability constant of this complex is 3.1×10^6.

$$[Cd(H_2O)_4]^{2+} + 2(en) \rightleftharpoons [Cd(en)_2]^{2+} + 4H_2O \quad (4.5)$$

The complex ion so formed is a chelate ion, which is shown below.



The stability constant of this complex is 3.2×10^{10}. It is clear from the values of stability constant that the chelate ion ($[Cd(en)_2]^{2+}$) is much more stable than the simple complex ion ($[Cd(CH_3NH_2)_4]^{2+}$). The greater stability of chelate ion can be explained in terms of thermodynamic changes as follows:

- A species can be stable, only when the value of standard free energy change (ΔG^o) is highly negative. Standard free energy change is given by: $\Delta G^o = \Delta H^o – T\Delta S^o$ where ΔH^o = Standard enthalpy change and ΔS^o = Standard entropy change

  The value of ΔG^o depends on ΔH^o and ΔS^o and hence stability depends on ΔH^o and ΔS^o. Greater the negative value of ΔH^o and positive value of ΔS^o, at constant T, higher is the negative value of ΔG^o. So, the species will be highly stable.
- The values of ΔH^o for the above two reactions are same. (i.e.,~ –57kJ).
- Hence, greater stability of $[(Cd(en)_2]^{2+}$is due to its greater positive value of standard entropy change (ΔS^o). The ΔS^o becomes positive when the randomness of the product side is greater

than that of reactant side. If the product side contains more number of species, its randomness will be greater.

- As shown in Eq. (4.4), four molecules of CH_3NH_2 displace four molecules of H_2O to form the complex ion $[Cd(CH_3NH_2)_4]^{2+}$. So the number of species in reactant side is equal to that of product side. This causes no change in the extent of randomness. In other words, there is no change in entropy ($\Delta S^o = 0$) in the formation of simple complex ion $[Cd(CH_3NH_2)_4]^{2+}$. Therefore, the value of ΔG^o for Eq. (4.4) depends only on ΔH^o, which has the same value for Eq. (4.5).
- In Eq. (4.5), two molecules of ethylenediamine displace four molecules of H_2O. As a result, the number of species in product side is more than that in reactant side. This causes increase in randomness. Thus, change in entropy (ΔS^o) for this reaction becomes positive. Consequently, ΔG^o will have a larger negative value. This accounts for the greater stability of chelate ion $[Cd(en)_2]^{2+}$.

2. A chelating ligand possesses more than one donation site, whereas a simple monodentate ligand possesses only one. When one end of the chelating ligand gets attached by one of its donation site with the central metal ion, the other site becomes very close to be attached with it. On the other hand, the simple monodentate ligand is attached to the central metal ion one by one. As a result, the formation of a complex with the monodentate ligand becomes difficult as compared to that of a chelate. Therefore, chelates are more stable than the simple complexes.

Concept Check

- Which among CN^- and NH_3 will form a more stable complex and why?
- What do you understand by the term chelate effect?
- Which of the following complex ion is more stable and why?
  $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$

4.5 Theories for Bonding in Coordination Compounds

Four theories have been postulated for the formation of coordination compounds.

Werner's Coordination Theory

The first systematic study on physical, chemical, structural and behavioral aspects of coordination compounds was done by Swiss chemist, Alfred Werner and he proposed his theory for coordination compounds in 1893. The main postulates of the theory are given as follows:

1. The metal ion encapsulated inside the coordination complex exhibits two types of valencies: **primary valency** and **secondary valency**.
2. The **primary valency** is ionizable as well as non-directional. It corresponds to the *oxidation state* in the modern-day terminology. Normally, if a complex ion exhibits positive charge, the primary valency corresponds to the number of charges present on the complex ion and this charge is balanced by the same number of negative ions. Thus, primary valency can also be defined by the number of anions neutralizing the charge on the complex ion. It is represented by a dotted line in the structure. Primary valency applies equally well to complexes as well as to simple salts. For example, nickel metal ion has primary valency 2 in the salt $NiCl_2$ as well as in the complex $[Ni(NH_3)_6]Cl_2$.
3. The **secondary valency** is directional, non-ionizable and corresponds to *coordination number* in the modern-day terminology. The total number of coordinate bonds formed between the central metal ion and ligands inside the coordination sphere is the secondary valency of the central metal ion

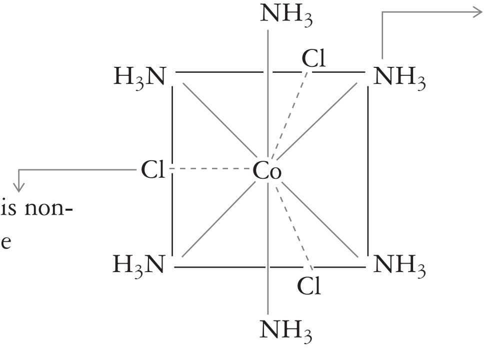
in the complex. It is represented by a solid line in the structure. The metal complex first satisfies its secondary valency and then its primary valency. Every metal ion has fixed number of secondary valencies, which are directed towards fixed positions in space around the central metal atom. This results in definite geometry and stereochemistry of the complex.

Based on this theory, Werner deduced and explained the structure of various cobalt amine complexes.

1. **$CoCl_3{\cdot}6NH_3$:** The central metal ion, cobalt, is in +3 oxidation state having primary valency of 3 and secondary valency (coordination number) of 6, which are satisfied, respectively, by three anionic Cl^- ligands and six neutral NH_3 ligands. The primary valencies represented by 3 Cl^- ions are ionizable as well as non-directional. This can be certified by the fact that on addition of $AgNO_3$, three equivalents of AgCl are obtained.

$$\underset{\text{Coordination complex}}{\overset{\substack{\text{Secondaty}\\ \text{valency}\\ \uparrow}}{[Co(NH_3)_6]}\quad \overset{\substack{\text{Primary}\\ \text{valency}\\ \uparrow}}{Cl_3}} + 2Ag^+ \longrightarrow \underset{\text{Complex ion}}{[Co(NH_3)_6]^{3+}} + \underset{\text{3 equivalents}}{3AgCl}$$

Six secondary valencies occupied by the neutral NH_3 ligands are directional in nature due to which the complex is formed with octahedral geometry. The octahedral geometry adopted by the complex can be represented as



Secondary valency which is directed towards fixed positions in space and is non-ionizable

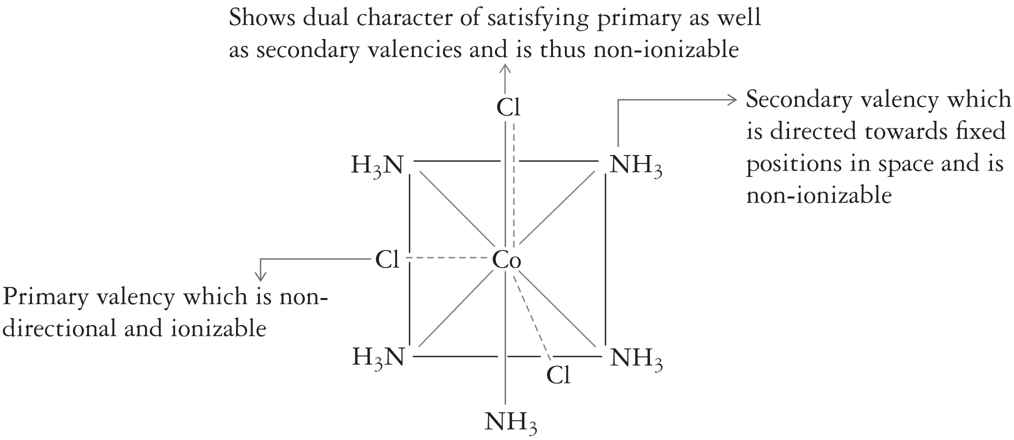
Primary valency which is non-directional and ionizable

$[Co(NH_3)_6]Cl_3$
(Yellow in color)

2. **$CoCl_3{\cdot}5NH_3$:** Here again cobalt ion has secondary valency as 6 and primary valency as 3. The secondary valency is satisfied with five neutral NH_3 ligands and one anionic Cl^- ligand, which has dual character and satisfies both primary as well as secondary valencies. The remaining primary valency of 2 is satisfied by 2 Cl^- ions.

$$\underset{\text{Coordination complex}}{\overset{\substack{\text{Secondary}\\ \text{valency}\\ \uparrow}}{[CoCl(NH_3)_5]}\quad \overset{\substack{\text{Primary}\\ \text{valency}\\ \uparrow}}{Cl_2}} + 2Ag^+ \longrightarrow \underset{\text{Complex ion}}{[CoCl(NH_3)_5]^{2+}} + \underset{\text{2 equivalents}}{2AgCl}$$

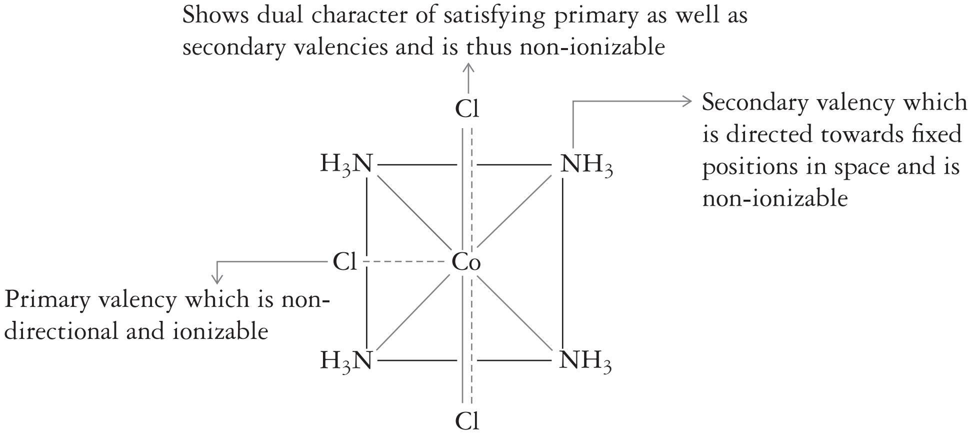
On addition of $AgNO_3$ only two equivalents of the AgCl will be obtained as the third Cl^- ion is satisfying primary as well as secondary valencies, and thus cannot be precipitated out. The octahedral structure of the complex can be represented as



$[CoCl(NH_3)_5]Cl_2$
(Purple in color)

3. **$CoCl_3 \cdot 4NH_3$:** Here two of the Cl^- ions exhibit dual character and satisfy both primary as well as secondary valencies. In this case, only one Cl^- will get precipitated out on addition of $AgNO_3$. The geometry exhibited by the coordination complex is again octahedral, with two spatial positions occupied by two Cl^- ions having dual character and the other four occupied by neutral NH_3 ligands.

$$\underset{\text{Coordination complex}}{\overset{\substack{\text{Secondary}\\ \text{valency}\\ \uparrow}}{[CoCl_2(NH_3)_4]}}\ \overset{\substack{\text{Primary}\\ \text{valency}\\ \uparrow}}{Cl} + Ag^+ \longrightarrow \underset{\text{Complex ion}}{[CoCl_2(NH_3)_4]^+} + \underset{\text{1 equivalent}}{AgCl}$$

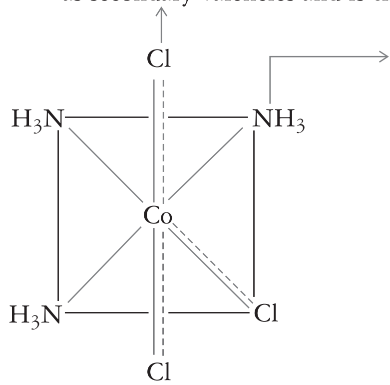


$[CoCl_2(NH_3)_4]Cl$
(Green in color)

4. **$CoCl_3 \cdot 3NH_3$:** Here all the three chloride ions are satisfying primary as well as secondary valencies, so none of the Cl^- ions can be precipitated out by addition of $AgNO_3$.

$$\underset{\text{Coordination complex}}{\overset{\substack{\text{Dual}\\ \text{character}\\ \uparrow}}{[CoCl_3(NH_3)_3]}} + Ag^+ \longrightarrow \text{No reaction}$$

The geometry of the complex is octahedral where three positions are occupied by the neutral NH_3 ligands and other three are occupied by the three anionic Cl^- ions.



Shows dual character of satisfying primary as well as secondary valencies and is thus non-ionizable

Secondary valency which is directed towards fixed positions in space and is non-ionizable

$[CoCl_3(NH_3)_3]$
(Violet in color)

Sidgwick Coordination Theory

Werner's coordination theory was further modified by Sidgwick using the Lewis concept of electron pair bond. It was based on the observation that each molecule or ion that coordinates to the central metal atom or ion has at least one unshared electron pair available for bond formation. The *donor* atom (ligand) donates the electron pair, while the *acceptor* atom (central metal ion) accepts this electron pair. The bond formed $M \leftarrow L$ is coordinate, dative and semipolar, where M is the acceptor metal ion that accepts both the electrons from the donor group L.

Sidgwick also made an observation that this tendency to accept electrons by the metal ion from the ligand atom continues till the total number of electrons in the metal ion is equal to the atomic number of noble gas element found in the same period in which the metal is situated. This total number of electrons represents the **effective atomic number (EAN)** of the metal and this rule is called the **18 electron rule**. By using this rule, it is possible to predict the number of ligands in the coordination compound and also the products of their reactions.

To obtain the EAN of a metal in a complex, we first subtract the number of electrons lost by the atom on ion formation from its atomic number, and then add the number of electrons gained through coordination with surrounding atoms. Mathematically it is calculated as follows:

$$\text{EAN} = Z(\text{Atomic number}) - \text{Oxidation number} + 2 \times \text{Number of ligands}$$

Let us take the example of $[Co(NH_3)_6]Cl_3$

1. The atomic number of cobalt is 27. Three electrons are lost in the formation of Co^{3+}, which means that the number of electrons in Co^{3+} is $27 - 3 = 24$.

2. Then, the six NH_3 ligands donate 2 electrons to the Co^{3+} ion, which means $6 \times 2 = 12$ electrons are contributed by 6 NH_3 ligands. Note that ligands in the primary valency will not contribute.
3. Adding the values obtained above, we get the EAN of cobalt as $24 + 12 = 36$.

Now this complex will be stable as per Sidgwick's theory because the number 36 corresponds to krypton, which is a noble gas. The EAN rule appears to hold good for most of the metal complexes with carbon monoxide and other ligands. However, there are some exceptions to the EAN theory, such as complexes with Ir^{4+}, Cr^{3+}, Pt^{2+}, Fe^{3+}, Pd^{2+}, Ni^{3+}, etc.

Valence Bond Theory

This theory was developed by Pauling and gave valence bond treatment to bonding in complexes. The main postulates of the theory are as follows:

1. For the coordinate bond formation between central metal ion and the ligand, the central metal ion makes available a number of empty orbitals; and the number of these empty orbitals is equal to the coordination number of the metal ion. For example, if the coordination number is 6, the central metal ion will make available six empty orbitals and if it is 4, the metal ion will make available four empty orbitals.
2. The atomic orbitals made available by the central metal ion will be a mixture of *s*, *p*, *d*-orbitals, all of which are of different energies and orientation. All these orbitals hybridize to give hybrid orbitals that are equivalent in energy and symmetry, which then form bonds with the ligands. These hybrid orbitals are directed along different directions in space due to which the complex acquires definite geometry like tetrahedral, square planar, octahedral, etc. (Table 4).

Table 4 Hybridization involved in complexes of different geometries

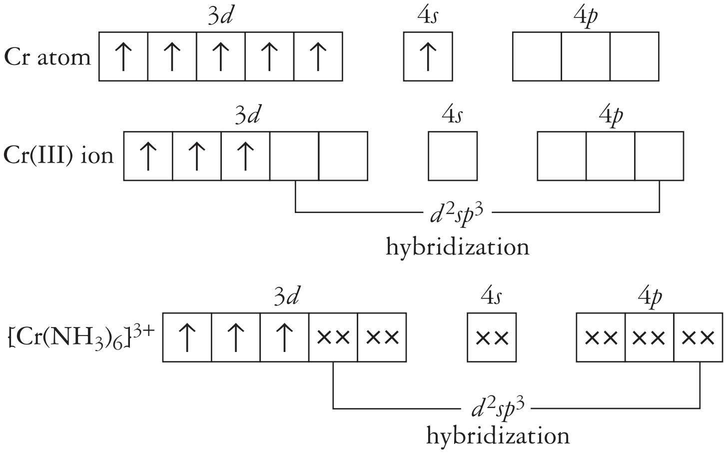
Coordination Number	*Hybridization Involved*	*Geometry*
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Square bipyramidal
6	sp^3d^2, d^2sp^3	Octahedral

3. The *d*-orbitals involved in hybridization can be either the inner *d*-orbital ($n - 1$) or the outer *d*-orbital (n). Accordingly, the complexes formed would be low spin and high spin, respectively.
4. Each ligand will have atleast one lone pair of electrons. It can have more than one pair of electrons to donate but should have atleast one.
5. The coordinate bond is formed when there is an overlap between hybridized empty orbitals of the central metal ion and filled orbitals of the ligand. The greater the extent of overlap, the stronger will be the bond and more stable will be the complex.
6. A complex is paramagnetic in nature if it contains unpaired electrons and is diamagnetic in nature if all the electrons in it are paired.
7. Presence of a strong-field ligand (discussed under Crystal Field Theory) causes the electrons to pair up against the Hund's rule of maximum multiplicity.

The valence bond theory could successfully explain the structure of a large number of coordination compounds. With the help of these postulates, we can predict the geometry of various coordination complexes. The following two examples illustrate the application of valence bond theory in the formation of octahedral and tetrahedral complexes.

Coordination Number 6

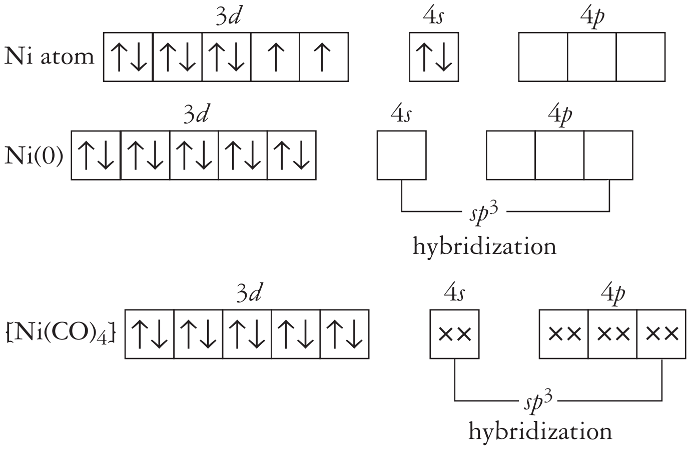
$[Cr(NH_3)_6]^{3+}$: Chromium atom ($Z = 24$) has electronic configuration of $3d^5\ 4s^1$. To achieve the oxidation state of +3 to form the complex, it loses one electron from $4s$ orbital and two electrons from $3d$ orbital, thereby generating Cr^{3+} ion. Two vacant $3d$, one $4s$ and three vacant $4p$ orbitals hybridize to give six equivalent d^2sp^3 hybrid orbitals which are directed towards six corners of a regular octahedron. Six pairs of electrons from six NH_3 molecules occupy these vacant orbitals and give rise to coordination number 6, and thus account for octahedral geometry for this complex.



Coordination Number 4

The compound with coordination number 4 could either be tetrahedral or square planar. Here we will discuss a simple example of tetrahedral complex.

$[Ni(CO)_4]$: In this complex, nickel is in zero(0) oxidation state with the configuration of $3d^8\ 4s^2$. The presence of CO, which is a very strong-field ligand, forces the electrons present in the $4s$ orbitals to pair up with the electrons in the $3d$ orbital. Thus, the empty $4s$ and $4p$ orbitals hybridize to form four equivalent sp^3 hybrid orbitals which are directed towards four corners of a regular tetrahedron. Four pairs of electrons from four carbonyl (CO) ligands occupy these vacant orbitals to form tetrahedral complex with coordination number 4. This is shown in the following figure:



Limitations of Valence Bond Theory

There are certain limitations of the valence bond theory:

1. It is only a qualitative explanation for bonding in coordination compounds.
2. It does not explain why some complexes are colored while others are not. The complex of same metal in the same oxidation state may have different colors with different ligands.
3. The magnetic and spectral properties of some of the complexes are not explained.
4. It does not explain the kinetic and thermodynamic stabilities of the coordination complexes.
5. The predictions given regarding the complexes having square planar and tetrahedral geometries are not exact.
6. The demarcation between strong-field and weak-field ligands (discussed in next section) is not proper.

Crystal Field Theory (CFT)

Crystal field theory was developed by H. Bethe and V. Bleck in 1935. It explained the nature of bonding between central metal ion and ligands in complex compounds. Magnetic and spectral properties of complex compounds were successfully explained by this theory. The salient features of this theory are as follows.

1. The bonding between a central metal ion and the ligands in a complex compound is purely electrostatic. The negatively charged ligands are attracted towards positively charged central metal ion due to electrostatic interactions. If the ligands are neutral molecules such as NH_3, H_2O etc., the negative end of dipole is attracted towards central positive ion. Ligands are considered as point charges in crystal field theory.
2. *d*-orbitals of central metal ion are divided into two groups depending on their orientation in space. One of the groups consists of three orbitals (d_{xy}, d_{yz} and d_{zx}), which are oriented in the regions in between the coordinate axes. These three orbitals are called non-axial orbitals. The other group comprises two orbitals ($d_{x^2-y^2}$, d_{z^2}) which are oriented along the coordinate axes. These two orbitals are called axial orbitals. All these five orbitals of a free metal ion have the same energy and hence are called degenerate *d*-orbitals. The orientations of *d*-orbitals of a free metal ion are shown in Figure 1.

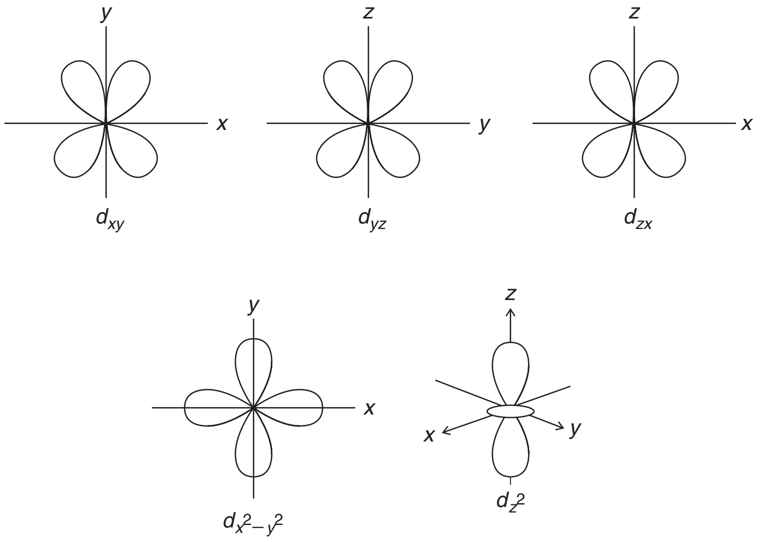


Figure 1 Orientations of five *d*-orbitals of a free metal ion.

3. The energy of *d*-orbitals of the central metal ion will increase uniformly when the central metal ion is spherically surrounded by a uniformly spread negative charges or ligands as shown in Figure 2. The five *d*-orbitals remain degenerate though they acquire higher energy. The increase in energy of these five degenerate *d*-orbitals is due to the electrostatic repulsion between the electrons in *d*-orbitals and the ligands.

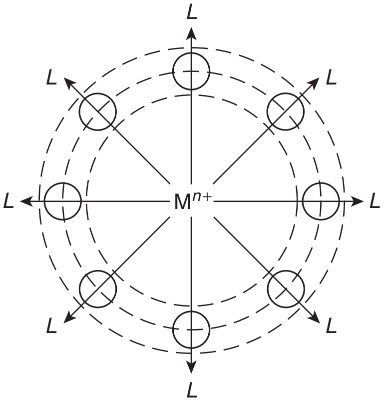


Figure 2 The central metal ion is surrounded by uniformly spread negative charges or ligands.

4. When the ligands approach to the central metal ion along a specific direction in a complex of definite geometry, the electrons present in those the *d*-orbitals which lie along these directions, experience more repulsion and the energy of these *d*-orbitals increase. As a result, degeneracy of five degenerate *d*-orbitals is lost and they split into two sets of different energies. Thus, the splitting of five degenerate *d*-orbitals of the central metal ion into two sets of orbitals having different energies in a given ligand environment or in a complex of definite geometry is called **crystal field splitting** which is shown in Figure 3. The energy gap between the two sets of *d*-orbitals is called **crystal field splitting energy** (Δ).

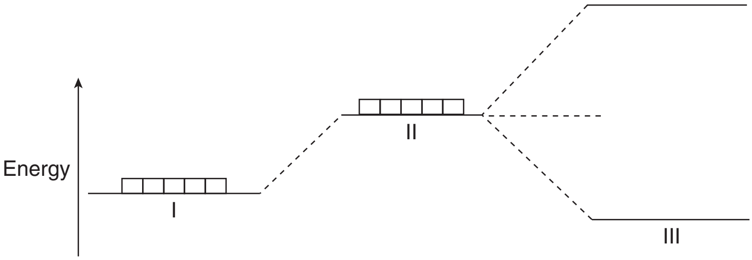


Figure 3 Crystal field splitting of *d*-orbitals of central metal ion of a complex in a given ligand environment.

State I represents degeneracy of all the five *d*-orbitals in the isolated or free metal ion. **State II** represents five degenerate *d*-orbitals with higher energy when the central metal ion is spherically surrounded by uniformly spread negative charges or ligands. **State III** represents crystal field splitting of five degenerate *d*-orbitals of central metal ion in a given ligand environment.

5. Electrons are filled in split *d*-orbitals in accordance with Aufbau principle, Hund's rule and Pauli's exclusion principle. It means that electrons are accommodated in various *d*-orbitals in increasing order of their energy. In other words, electron enters first into the orbital having minimum energy. Pairing of electrons takes place only when all the orbitals of a given set

are filled with at least one electron each. Electrons remain in paired form in an orbital with their opposite spin.

6. The magnitude of crystal field splitting depends on geometry of the complex,magnitude of charge on the central metal ion and strength of ligands.

Factors Affecting the Magnitude of Crystal Field Splitting

Magnitude of crystal field splitting in various complexes is not the same. It depends on nature of ligands, oxidation state of the central metal ion, size of *d*-orbitals of the central metal ion and geometry of the complexes. These are discussed as follows.

1. **Nature of ligands:** Greater the ease with which ligands are attracted towards the central metal ion, the larger is the crystal field splitting in a complex compound. Ligands with negative charge of high magnitude, small size, having strong tendency to donate sigma (σ) electrons and to accept pi (π) electrons, produce large crystal field splitting as these are strongly attracted by the central metal ion.

   Therefore, ligands can be arranged in increasing order of their power to produce crystal field splitting. This arrangement of ligands is called **spectrochemical series** which is given as follows.

$$I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- < OX^{2-} < H_2O < EDTA < py \approx NH_3 < en < NO_2^- < CN^- < CO$$

   The ligands which produce small crystal field splitting such as I^-, Br^-, etc. are known as weak field ligands and those which produce large crystal field splitting such as CO, CN^-, etc. are called strong field ligands.

2. **Oxidation state of the central metal ion:** The metal ion with high oxidation state causes larger crystal field splitting. For example, crystal field splitting energy (Δ_o) for $[Co(H_2O)_6]^{3+}$ is 18600 cm^{-1} whereas that for $[Co(H_2O)_6]^{2+}$ is 9300 cm^{-1}. It is because the central metal ion in first complex ion carries +3 magnitude of charge while that in the second complex ion is +2.
3. **Size of *d*-orbitals of the central metal ion:** If the size of *d*-orbitals of the penultimate shell of the central metal ion in a complex is large, the extent of crystal field splitting becomes higher. It is because *d*-orbitals having larger size are extended farther into space. This causes strong interaction of *d* electrons with the ligands and hence larger crystal filed splitting occurs. For example, the crystal field splitting in $[Co(NH_3)_6]^{3+}$ is 23,000 cm^{-1} while that in $[Rh(NH_3)_6]^{3+}$ is 34,000 cm^{-1}. In the first case, the central metal ion is Co^{3+}, which has 3*d* orbitals. The central metal ion in the second case is Rh^{3+} which as 4*d* orbitals. Since size of 4*d* orbitals is larger than that of 3*d* orbitals, crystal field splitting in $[Rh(NH_3)_6]^{3+}$ is greater than that in $[Co(NH_3)_6]^{3+}$.
4. **Geometry of the complexes:** Crystal field splitting also depends on geometry of the complex. For example, crystal field splitting in tetrahedral complexes is smaller in comparison to that in octahedral complexes.

Concept Check

- Identify the primary and secondary valencies in the following complexes:

  $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4Cl_2]Cl$, $[CoCl_3(NH_3)_3]$.

- Out of the primary and secondary valencies, which valency will determine the geometry and stereochemistry of the complex?
- What do you understand by the term effective atomic number (EAN) proposed by Sidgwick?

What is the EAN of metal ion in the complex $[Co(NH_3)_6]Cl_3$?
- What is the hybridization of metal atom in the complex $[Co(NH_3)_6]Cl_3$?
- How do weak and strong field ligands differ in terms of crystal field splitting energy? Which among the following is the most strong-field ligand Cl^-, NO_2^-, CN^-, CO?
- How does crystal field splitting vary with oxidation state and size of *d*-orbitals of a central metal ion?

4.6 Crystal Field Splitting in Octahedral and Tetrahedral Complexes

The magnitude of crystal field splitting depends on geometry of complexes. So crystal field splitting in octahedral complexes is different from that in tetrahedral complexes. We will now study crystal field splitting in octahedral and tetrahedral complexes and various factors determining arrangement of electrons and their effect on properties of complexes.

Octahedral Complexes

1. The coordination number of the central metal ion in an octahedral complex is six. In this complex, the central metal ion is at the center and the ligands occupy the six corners of a regular octahedron as shown in Figure 4. All the three coordinate axes X, Y and Z pass six corners of the octahedron.

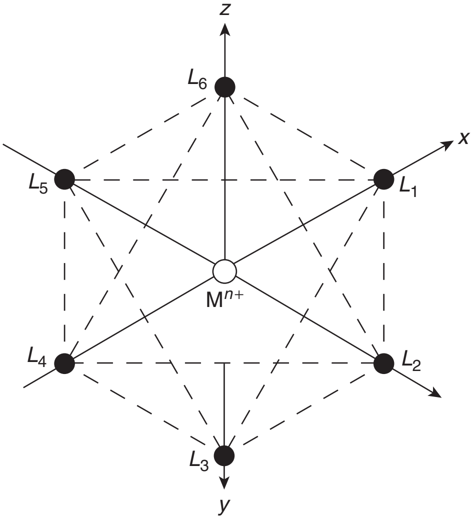


Figure 4 Central metal ion is surrounded by six ligands in an octahedral complex.

2. As shown in Figure 4, six ligands approach to central metal ion along three coordinate axes. Hence, electrons present in two axial orbitals ($d_{x^2-y^2}$, d_{z^2}) experience more repulsion from the ligands as compared to the other three non-axial orbitals (d_{xy}, d_{yz}, d_{zx}). As a result, the energy of the two axial orbitals increases. This causes splitting of five degenerate *d*-orbitals into two sets of different energies. This

splitting of *d*-orbital is known as crystal field splitting in an octahedral complex or in an octahedral ligand field. It is shown in Figure 5. The two axial orbitals are called e_g orbitals and three non-axial orbitals are known as t_{2g} orbitals.

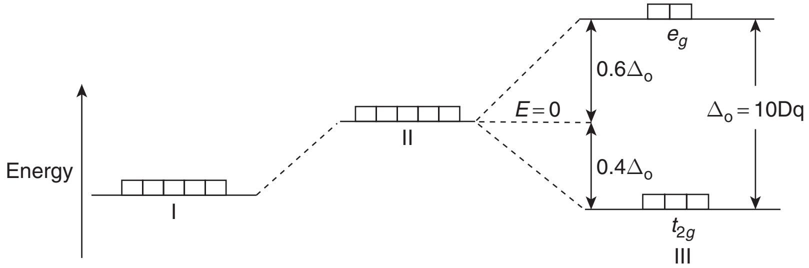


Figure 5 Crystal field splitting of *d*-orbitals in an octahedral complex or in an octahedral ligand environment.

State I represents degeneracy of all the five *d*-orbitals in the isolated or free metal ion. **State II** represents five degenerate *d*-orbitals with higher energy when the central metal ion is spherically surrounded by uniformly spread negative charges or ligands. **State III** represents crystal field splitting of five degenerate *d*-orbitals of central metal ion in an octahedral complex.

3. The energy difference between these two set of *d*-orbitals (i.e., t_{2g} and e_g) is called crystal field splitting energy, which is denoted by Δ_o. It is generally calculated in terms of Dq. By convention one Δ_o is taken as 10Dq. The letter "o" represents octahedral complex.
4. Electrons are filled in different set of *d*-orbitals in increasing order of energy. Suppose a free metal ion contains one electron in *d*-orbital of penultimate shell. That electron goes to any one of the t_{2g} orbitals when an octahedral complex is formed. In such a case, *d*-orbital configuration is written as t_{2g}^1, e_g^0.
5. Each electron entering into t_{2g} orbital, causes decrease in energy by 4Dq or $0.4\Delta_o$. Decrease in energy is usually denoted by a *negative sign*. Similarly, each electron entering in to e_g orbital, causes increase in energy by 6Dq or $0.6\Delta_o$. Increase in energy is usually denoted by a *positive sign*.
6. If the central metal ion in an octahedral complex contains one electron in t_{2g} orbital, its energy is decreased by $1 \times (-0.4\Delta_o) = -0.4\Delta_o$.This decrease in energy of the central metal ion is called **crystal field stabilization energy (CFSE)** since decrease in energy corresponds to increase in stability of species. *Thus CFSE may be defined as the lowering in the energy of a transition metal ion in a* ***given ligand environment due to crystal field effects***. The splitting of *d*-orbitals of a metal ion due to electrostatic crystal field potential of ligands and the consequences thereof are known as crystal field effects.
7. Crystal field stabilization energy depends on number of electrons present in t_{2g} and e_g orbitals. For example, if a central metal ion contains two electrons in *d*-orbitals of penultimate shell in an octahedral complex (i.e., d^2 system), those two electrons enter into t_{2g} orbitals. So, the *d*-orbital configuration can be written as t_{2g}^2, e_g^0. In this case, CFSE of the central metal ion is $2 \times (-0.4\Delta_o) = -0.8\Delta_o$. Similarly, for a d^3 octahedral system, the *d*-orbital configuration can be written as t_{2g}^3, e_g^0 and CFSE of the central metal ion is $3\times(-0.4\Delta_o) = -1.2\,\Delta_o$.
8. For d^4 system there are two possibilities of arrangement of electrons and hence there are two values of CFSE.

Case I: All the four electrons may be accommodated in t_{2g} orbitals. In such a case, the *d*-orbital configuration is written as: $\boldsymbol{t_{2g}^4 e_g^0}$. It is shown in Figure 6.

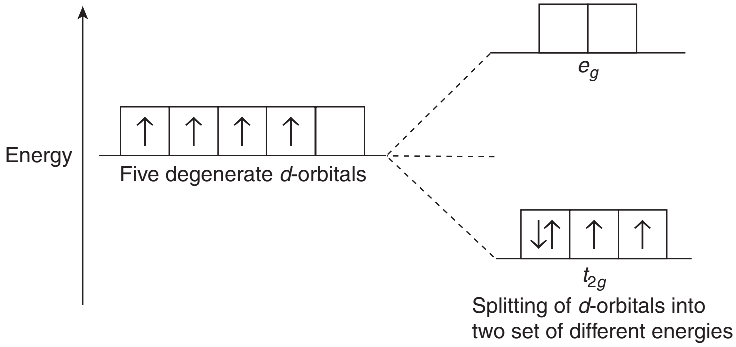


Figure 6 Arrangement of four electrons in t_{2g} orbitals of the central metal ion in an octahedral complex.

Case II: Three electrons may be accommodated in t_{2g} orbitals and one electron goes to one of the e_g orbitals. In such a case, *d*-orbital configuration is written as: $\boldsymbol{t_{2g}^3 e_g^1}$. It is shown in Figure 7.

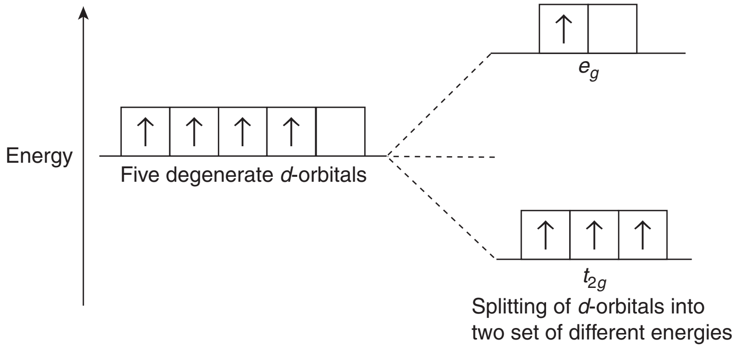


Figure 7 Arrangement of four electrons in t_{2g} and e_g orbitals of the central metal ion in an octahedral complex.

The actual configuration is decided on the basis of the value of Δ_o and pairing energy (*P*). Pairing energy is the energy required to pair the electrons in one orbital. It is related to the energy of electrostatic repulsion among *d*-electrons.

In case pairing energy is less than that of crystal field splitting energy (Δ_o), electrons prefer to be paired. This occurs in Case I. Thus configuration (I) is followed when the value of crystal field splitting energy (Δ_o) becomes greater than pairing energy (*P*). Δ_o becomes larger, if repulsion between the ligands and central metal ion in the complex is higher. Strong-field ligands such as CO, CN^-, NH_3, etc. cause larger repulsion. In other words, Δ_o becomes larger when the complex contains strong-field ligands. Such complexes are called **strong-field complexes**. Hence, configuration (I) is followed for strong-field octahedral complex. Since electrons prefer to be paired in strong-field complexes, the number of unpaired electrons (spin) is relatively less. So, strong-field octahedral complexes are also called **low-spin octahedral complexes**.

In case crystal field splitting energy (Δ_o) is less than that of pairing energy, electrons prefer to go to e_g orbitals, when t_{2g} orbitals get half-filled. Since pairing energy is higher, electrons do not prefer to be paired. So, configuration (II) is followed. In this case, the number of unpaired electrons (spin) becomes more and hence such complexes are called **high-spin complexes**.

If crystal field splitting energy is less, the central metal ion experiences less repulsion from the ligands. Usually, weak-field ligands such as F^-, Cl^-, etc. cause less repulsion and hence the octahedral complexes containing weak-field ligands are called weak-field octahedral complexes.

Crystal field stabilization energy (CFSE) for Case II (i.e., $t_{2g}^3e_g^1$) is calculated as: $3 \times (-0.4\Delta_o) + 1 \times (0.6\Delta_o) = -0.6\Delta_o$. Similarly, CFSE for Case I is calculated to be $4 \times (-0.4\Delta_o) = -1.6\Delta_o$. However, the observed CFSE for Case I (i.e., $t_{2g}^4e_g^0$) will be less than that of the calculated value. It is because there occurs repulsion between two paired electrons, which is called interelectronic repulsion. Some amount of energy equal to pairing energy is consumed from CFSE to minimize this repulsion. It is difficult to calculate pairing energy. In order to avoid this difficulty, CFSE is calculated by neglecting interelectronic repulsions. So, CFSE for $t_{2g}^4e_g^0$ configuration is considered to be $-1.6\Delta_o$ by neglecting interelectronic repulsions. CFSE is calculated similarly for other systems which contain paired electrons.

9. The CFSE for metal ions having different number of *d*-electrons in octahedral complexes are given in Table 5.

Table 5 *d*-orbital configuration and CFSE values in weak field and strong field octahedral complexes

Number of d-electrons	*Electronic Configuration of Split d-orbitals in Weak Field or High-Spin Octahedral Complexes*	*CFSE*	*Electronic Configuration of Split d-orbitals in Strong Field or Low-Spin Octahedral Complexes*	*CFSE*
1	$t_{2g}^1e_g^0$	$1 \times (-0.4\Delta_o) = -0.4\Delta_o$	$t_{2g}^1e_g^0$	$-0.4\Delta_o$
2	$t_{2g}^2e_g^0$	$2 \times (-0.4\Delta_o) = -0.8\Delta_o$	$t_{2g}^2e_g^0$	$-0.8\Delta_o$
3	$t_{2g}^3e_g^0$	$3 \times (-0.4\Delta_o) = -1.2\Delta_o$	$t_{2g}^3e_g^0$	$-1.2\Delta_o$
4	$t_{2g}^3e_g^1$	$3 \times (-0.4\Delta_o) + 1 \times (0.6\Delta_o) = -0.6\Delta_o$	$t_{2g}^4e_g^0$	$4 \times (-0.4\Delta_o) = -1.6\Delta_o$
5	$t_{2g}^3e_g^2$	$3 \times (-0.4\Delta_o) + 2 \times (0.6\Delta_o) = 0.0\Delta_o$	$t_{2g}^5e_g^0$	$5 \times (-0.4\Delta_o) = -2.0\Delta_o$
6	$t_{2g}^4e_g^2$	$4 \times (-0.4\Delta_o) + 2 \times (0.6\Delta_o) = -0.4\Delta_o$	$t_{2g}^6e_g^0$	$6 \times (-0.4\Delta_o) = -2.4\Delta_o$
7	$t_{2g}^5e_g^2$	$5 \times (-0.4\Delta_o) + 2 \times (0.6\Delta_o) = -0.8\Delta_o$	$t_{2g}^6e_g^1$	$6 \times (-0.4\Delta_o) + 1 \times (0.6\Delta_o) = -1.8\Delta_o$
8	$t_{2g}^6e_g^2$	$6 \times (-0.4\Delta_o) + 2 \times (0.6\Delta_o) = -1.2\Delta_o$	$t_{2g}^6e_g^2$	$6 \times (-0.4\Delta_o) + 2 \times (0.6\Delta_o) = -1.2\Delta_o$
9	$t_{2g}^6e_g^3$	$6 \times (-0.4\Delta_o) + 3 \times (0.6\Delta_o) = -0.6\Delta_o$	$t_{2g}^6e_g^3$	$6 \times (-0.4\Delta_o) + 3 \times (0.6\Delta_o) = -0.6\Delta_o$
10	$t_{2g}^6e_g^4$	$6 \times (-0.4\Delta_o) + 4 \times (0.6\Delta_o) = 0.0\Delta_o$	$t_{2g}^6e_g^4$	$6 \times (-0.4\Delta_o) + 4 \times (0.6\Delta_o) = 0.0\Delta_o$

Tetrahedral Complexes

1. The coordination number of a complex compound with tetrahedral geometry is 4. All the four ligands in a tetrahedral complex occupy four alternate corners of a cube in which the central metal ion is placed at the center as shown in Figure 8.

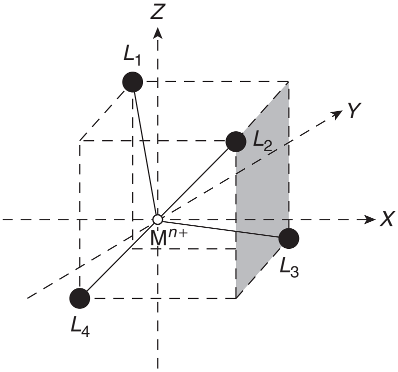


Figure 8 Central metal ion is surrounded by four ligands in a tetrahedral complex.

2. In Figure 9, State I represents degeneracy of all five *d*-orbitals in the isolated metal atom or ion and State II represents *d*-orbitals with higher energy when surrounded uniformaly by ligands. In a tetrahedral complex, the ligands approach to the central metal ion in between the coordinate axes which is shown in Figure 8. So, the electrons present in d_{xy}, d_{yz} and d_{zx} orbitals, which have orientations in between the coordinate axes, will experience more repulsion from the ligands.This causes the increase in energy of these three orbitals. As a result, five degenerate *d*-orbitals of the central metal ion are split into two sets of orbitals. This splitting of *d*-orbitals of the central metal ion in the presence of tetrahedral ligand field is known as crystal field splitting in tetrahedral complex. It is shown in State III in Figure 9.

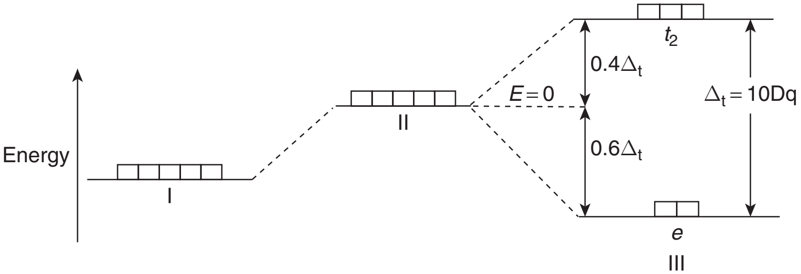


Figure 9 Crystal field splitting of *d*-orbitals in a tetrahedral complex or in a tetrahedral ligand environment.

3. The energy of d_{xy}, d_{yz} and d_{zx} orbitals of the central metal ion is more than that of $d_{x^2-y^2}$ and d_{z^2} orbitals in a tetrahedral complex due to crystalfield splitting. The d_{xy}, d_{yz} and d_{zx} are designated as *e* orbitals, whereas $d_{x^2-y^2}$ and d_{z^2} are designated as t_2 orbitals.
4. The energy difference between *e* and t_2 orbitals is known as crystal field splitting energy in tetrahedral complex, which is denoted by Δ_t. Here t stands for tetrahedral complex. Crystal field splitting energy in tetrahedral complex (Δ_t) is less than that in octahedral complex (Δ_o). It has been observed

that $\Delta_t \approx -4/9\Delta_o$. Negative sign (–) indicates that splitting in tetrahedral complex is just reverse of that in octahedral complex. The small value of Δ_t is partly due to the presence of less number of ligands in tetrahedral complex as compared to that in octahedral complex. By convention, Δ_t is taken as 10Dq.

5. Since an electron prefers to move into a region of lower energy for reasons of stability, the electrons are accommodated first in *e* orbitals and then in t_2 orbitals in a tetrahedral complex.
6. Each electron entering into *e* orbital is stabilized by $0.6\Delta_t$ or 6Dq while that coming into t_2 orbital is destabilized by $0.4\Delta_t$ or 4Dq.
7. All tetrahedral complexes form high-spin configuration. This is due to the fact that crystal field splitting in tetrahedral complex is quite small and is always less than the pairing energy. Therefore, electrons prefer to remain unpaired by moving to t_2 orbitals. Since number of unpaired electrons (spin) is more, all tetrahedral complexes are high-spin complexes.
8. *d*-orbital configuration and crystal field stabilization energy (CFSE) of central metal ion containing different number of *d*-electrons in tetrahedral complexes are given in Table 6.

Table 6 *d*-orbitals configuration and crystal field stabilization energy (CFSE) of central metal ion containing different number of *d*-electrons in tetrahedral complexes.

Number of d-electrons	*Electronic Configuration of Split d-orbitals in Tetrahedral Complexes*	*CFSE*
1	$e^1t_2^0$	$1 \times (-0.6\Delta_t) = -0.6\Delta_t$
2	$e^2t_2^0$	$2 \times (-0.6\Delta_t) = -1.2\Delta_t$
3	$e^2t_2^1$	$2 \times (-0.6\Delta_t) + 1 \times (0.4\Delta_t) = -0.8\Delta_t$
4	$e^2t_2^2$	$2 \times (-0.6\Delta_t) + 2 \times (0.4\Delta_t) = -0.4\Delta_t$
5	$e^2t_2^3$	$2 \times (-0.6\Delta_t) + 3 \times (0.4\Delta_t) = 0.0\Delta_t$
6	$e^3t_2^3$	$3 \times (-0.6\Delta_t) + 3 \times (0.4\Delta_t) = -0.6\Delta_t$
7	$e^4t_2^3$	$4 \times (-0.6\Delta_t) +3 \times (0.4\Delta_t) = -1.2\Delta_t$
8	$e^4t_2^4$	$4 \times (-0.6\Delta_t) + 4 \times (0.4\Delta_t) = -0.8\Delta_t$
9	$e^4t_2^5$	$4\times (-0.6\Delta_t) + 5 \times (0.4\Delta_t) = -0.4\Delta_t$
10	$e^4t_2^6$	$4\times (-0.6\Delta_t) + 6 \times (0.4\Delta_t) = 0.0\Delta_t$

Concept Check

- According to crystal field theory, how do five degenerate *d*-orbitals split in the presence of ligands in octahedral complexes?
- Crystal field splitting in tetrahedral complexes is $(\Delta_t) = -4/9\ \Delta_o$. Explain.
- Strong field ligands lead to the formation of low-spin complexes. Explain.

4.7 Applications of Crystal Field Theory

Crystal field theory explains the magnetic and spectral properties of complex compounds. These are discussed as follows.

Magnetic Properties of Complexes

1. If a substance possesses paired electrons, the magnetic moment of one electron is cancelled by the equal and opposite magnetic moment of the other. Such substance gets repelled from an external magnetic field and are called **diamagnetic** substances. Similarly, a substance having one or more unpaired electrons possesses a definite magnetic moment and is attracted by an external magnetic field. Such substances are said to be **paramagnetic**.
2. Greater the number of unpaired electrons, higher is the magnetic moment of the substance. Magnetic moment (μ) of a substance can be calculated as follows.

$$\mu = \sqrt{n(n+2)}$$

   where n is the number of unpaired electrons.
   Magnetic moment is expressed in Bohr Magneton (BM).
3. The magnetic behavior of complexes can be explained by crystal field theory. For example, $[Co(NH_3)_6]^{3+}$ is diamagnetic whereas $[CoF_6]^{3-}$ is paramagnetic though the central metal ion is Co^{3+} in both the cases.
4. Ammonia molecules are considered as strong-field ligands. So a strong-field ligand environment is prevailed in $[Co(NH_3)_6]^{3+}$. As a result of which, crystal field splitting of 3*d* orbitals of Co^{3+} ion becomes larger. In other words, crystal field splitting energy (Δ_o) is greater than the pairing energy (P). Therefore, all the six *d* electrons of Co^{3+} remain in three t_{2g} orbitals in the octahedral $[Co(NH_3)_6]^{3+}$ ion. Splitting of *d*-orbitals of $Co^{3+}$and arrangement of these electrons in split *d*-orbitals are shown in Figure 10.

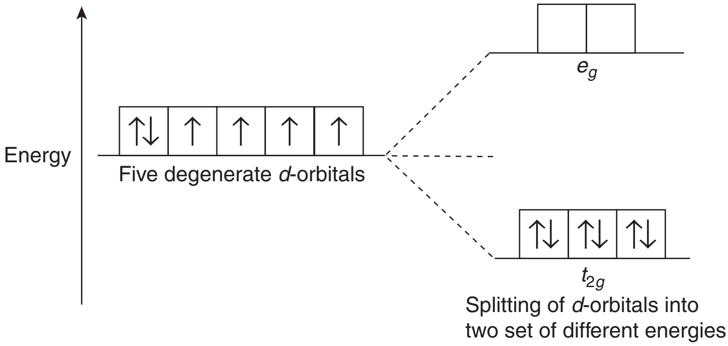


Figure 10 Arrangement of all six electrons of 3*d* orbitals of Co^{3+} ion in t_{2g} orbitals in $[Co(NH_3)_6]^{3+}$ ion.

   It is known from Figure 10 that there is no unpaired electron in $[Co(NH_3)_6]^{3+}$ and its magnetic moment is zero. So this complex ion is diamagnetic.
5. Similarly, fluoride ion (F^-) is considered as a weak-field ligand. This produces a weak field octahedral complex ion $[CoF_6]^{3-}$ due to which crystal field splitting of *d*-orbitals of Co^{3+} becomes

smaller. So crystal field splitting energy (Δ_o) is less than pairing energy (P). Splitting of d-orbitals of Co^{3+} and arrangement of these electrons in split d-orbitals are shown in Figure 11.

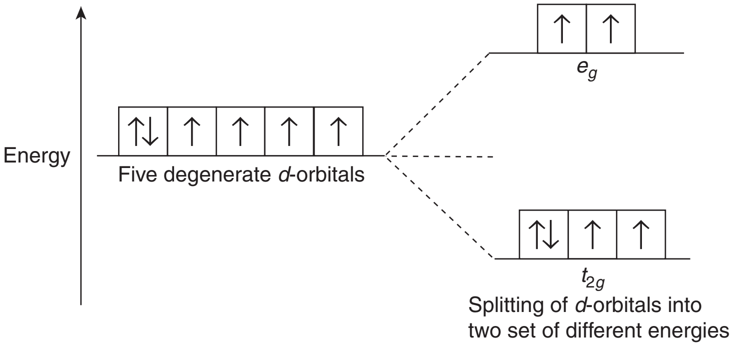


Figure 11 Arrangement of all six electrons of $3d$ orbitals of Co^{3+} ion in t_{2g} and e_g orbitals in $[CoF_6]^{3-}$ion.

The first three d-electrons are accommodated in t_{2g} orbitals while fourth and fifth d electrons enter into e_g orbitals. The sixth electron comes to one of the three t_{2g} orbitals. As a result, four unpaired electrons are present due to which this complex ion becomes paramagnetic. Its magnetic moment can be calculated as: $\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.8989$ BM

Color of Complexes

1. When visible light is allowed to fall on a complex, any one of the following three cases occur:
   - The complex may absorb the whole visible light. In this case, the complex appears black.
   - The complex may transmit all the visible light. In such case, complex appears white.
   - The complex may absorb light of a definite wavelength from the visible region and the remaining portion of it gets transmitted due to which the complex appears colored. The color of the complex is same as the color of transmitted light which is called complimentary color of the absorbed color. Color of the absorbed light is different from that of transmitted light. For example, if violet color from visible light is absorbed, yellow color is transmitted and the complex appears yellow. Thus, yellow color is the complimentary color of violet color. Different components of visible light and their complementary colors are given in Table 7.

Table 7 Wavelength range and complementary color of absorbed color

Absorbed Color	*Wavelength Range(Å) of Absorbed Color*	*Complementary Color*
Violet	4000–4500	Yellow
Blue	4500–5000	Orange
Green	5000–5500	Red
Yellow	5500–6000	Violet
Orange	6000–6500	Blue
Red	6500–7000	Green

2. A complex appears colored by absorbing suitable energy from **visible light**, if its central metal ion possesses incompletely filled *d*-orbitals. According to crystal field theory, *d*-orbitals of central metal ion in a complex are split into two sets of different energies. Energy gap between these two set of *d*-orbitals is very small. By absorbing suitable amount of energy from visible light, unpaired electron present in lower energy *d*-orbital jumps to higher energy *d*-orbital. This transition of *d* electron is called ***d-d* transition**. As a result of *d-d* transition, some amount of energy from visible region is absorbed and rest is transmitted, which gives the color of the complex. Let us consider an example to explain the color of a complex in which central metal ion contains incompletely filled *d*-orbitals. Such an example is aqueous solution of Ti^{3+} ions which is purple in color because of following reasons:
   - Aqueous solution of Ti^{3+} ion forms an octahedral complex ion having formula $[Ti(H_2O)_6]^{3+}$.
   - The central metal ion (Ti^{3+}) contains only one electron in *d*-orbitals of third shell (penultimate shell).
   - In presence of octahedral ligand field, the five degenerate *d*-orbitals of Ti^{3+} split into two sets of orbitals known as t_{2g} and e_g. The only *d*-electron is accommodated in lower energy t_{2g} orbital which is shown in Figure 12.
   - By absorbing energy from green and yellow region ($\lambda = 5000$ Å) of visible light, it is excited to e_g orbital of higher energy as shown in Figure 12. Other colors of visible region are transmitted together to produce purple color as complimentary color. As a result, aqueous solution of Ti^{3+} ion appears purple.

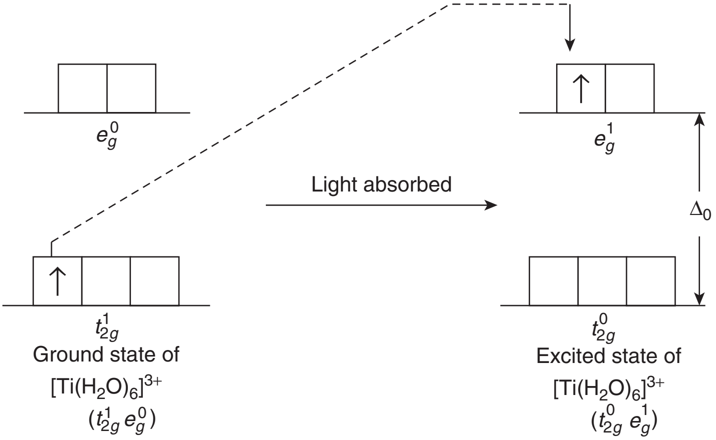


Figure 12 Excitation (*d-d* transition) of only *d* electron of Ti^{3+} in its aqueous solution from t_{2g} orbital to e_g orbital by absorbing suitable amount of energy from the visible region ($\lambda = 5000$ Å).

3. If a complex ion absorbs light of wavelength (infrared region) greater than visible light, it appears colorless. Similarly, if a complex ion absorbs light of wavelength (ultraviolet region) less than visible light, it also appears colorless. For example, anhydrous copper sulphate ($CuSO_4$) is colorless, since it absorbs light in infrared region and $[Cu(CN)_4]^{2-}$ ion is colorless as it absorbs in ultraviolet region.
4. Color of a complex depends on its **geometry**. For example, octahedral hydrated Co(II) complex $[Co(H_2O)_6]^{2+}$ appears pink while tetrahedral halo (fluoro, chloro, etc.) complexes of Co(II) $[CoX_4]^{2-}$ appear blue. It can be explained as follows:
   - Crystal field splitting energy (Δ_o) of octahedral hydrated Co(II) complex is larger than that of tetrahedral halo complexes of Co (II). As a result, the former requires higher energy from visible

region for *d-d* transition than that is required by the latter. Hence, highly energetic blue light is absorbed by octahedral hydrated Co(II) complex and it transmits less energetic pink colored light, which is the complimentary color of blue light. This causes the complex to appear pink.

- On the other hand, tetrahedral halo complexes of Co(II) absorb energy from red region (less energy) due to smaller crystal field splitting energy (Δ_t) and transmit highly energetic blue light due to which these complexes appear blue.

5. **Strength of ligands** are also responsible for color of complexes. For example, color of $[Co(NH_3)_6]^{3+}$ ion is orange whereas that of $[Co(CN)_6]^{3-}$ ion is yellow though both the ions possess same octahedral geometry and same central metal ion with identical configuration of *d*-orbitals. This is explained as follows.
   - CN^- ions are relatively stronger ligands as compared to NH_3 molecules. Stronger ligands cause large crystal filed splitting. So, the crystal field splitting energy in $[Co(CN)_6]^{3-}$ ion is larger than that in $[Co(NH_3)_6]^{3+}$.
   - As a result, *d-d* transition in $[Co(CN)_6]^{3-}$ requires higher energy from visible light and it absorbs energy from violet region due to which less energetic yellow light is transmitted. So this complex ion appears yellow.
   - On the other hand, relatively less energy is required for *d-d* transition in $[Co(NH_3)_6]^{3+}$ ion. So energy from blue region is absorbed and orange color is transmitted as the complementary color. This causes the color of $[Co(NH_3)_6]^{3+}$ ion to appear orange.
6. If the central metal ion in a complex, possesses **no d-electrons** *or* **completely filled d-orbitals**, *d-d* transition cannot be possible by the absorption of visible light and hence such complexes appear colorless or white. Due to this, complexes of $Cu^+(d^{10})$, $Zn^{2+}(d^{10})$, Ag^+ (d^{10}), $Cd^{2+}(d^{10})$, $Ti^{4+}(d^0)$, $Sc^{3+}(d^0)$, etc., are colorless.

Concept Check

- Calculate the magnetic moment of $[Ni(NH_3)_6]Cl_2$ and predict its magnetic behavior.
- Hydrated $CuSO_4$ appears blue whereas anhydrous $CuSO_4$ is colorless. Explain.
- Most of the transition metal complexes are colored in their solution or solid state. Why?

Key Terms

Coordination compound or complex compound

Double salt

Central metal ion

Ligand

Coordination number

Monodentate ligand

Bidentate ligand

Polydentate ligand

Chelate

Werner's coordination theory

Sidgwick coordination theory

Valence bond theory

Crystal field theory

Primary valency

Secondary valency

Effective atomic number

Crystal filed splitting of *d*-orbitals

Octahedral complex

Tetrahedral complex

Diamagnetic

Paramagnetic

d-d transition

Configuration of *d*-orbitals

Objective-Type Questions

Multiple-Choice Questions

1. The EAN of iron in $[Fe(CN)_6]^{4-}$ is
   - a. 34
   - b. 36
   - c. 37
   - d. 35
2. The oxidation number of cobalt in $[Co(NH_3)_5ONO]^{2+}$ is
   - a. +1
   - b. +2
   - c. +3
   - d. +4
3. Which of the following is the weakest ligand?
   - a. H_2O
   - b. OH^-
   - c. NH_3
   - d. I^-
4. The IUPAC name of $[Ni(CO)_4]$ is
   - a. tetracarbonylnickel(I)
   - b. tetracarbonylnickel(0)
   - c. tetracarbonylnickel(II)
   - d. tetracarbonylnickel(III)
5. $K_3[AI(C_2O_4)_3]$ is called
   - a. potassiumaluminooxalate.
   - b. potassiumalumino(III) oxalate.
   - c. potassiumtrioxalatoaluminate.
   - d. potassiumtrioxalatoaluminate(III)
6. Which of the following complex is expected to be a paramagnetic complex?
   - a. $[Ni(H_2O)_6]^{2+}$
   - b. $[Co(NH_3)_6]^{3+}$
   - c. $[Ni(CO)_4]$
   - d. $[Ni(CN)_4]^{2-}$

Fill in the Blanks

1. The addition compounds that lose their identity in solution are called _____ and those which retain their identity are called ________.
2. The number of ligands bound around a metal ion is called the ______ of the metal ion.
3. The atom of the ligand directly attached to the metal is called _____.
4. Ligands remove the degeneracy of ________ of the metal ion.
5. In the presence of ligands, *d*-orbitals of central metal ion exhibiting an octahedral geometry split into lower energy state _____ and higher energy state _______.

Review Questions

Short-Answer Questions

1. Why is chelate complex of a metal ion more stable than a simple complex of the same metal ion?
2. All coordination compounds with tetrahedral geometry are high-spin complexes. Give reason.
3. Why do transition metals form complexes?
4. Calculate the magnetic moment of the following complexes on the basis of crystal field theory.
   - a. $[CoCl_4]^{2-}$
   - b. $[Cr(en)_3]^{3+}$

5.

Complex	*Pairing Energy (P), cm^{-1}*	Δ_o, *cm^{-1}*
$[Co(H_2O)_6]^{3+}$	18,000	14,100
$[Co(CN)_6]^{3-}$	18,000	22,000

From the above table, predict whether the complexes will be low spin or high spin with proper explanation.

6. Name the complexes: $K_3[Cr(CN)_6]$ and $Na_2[ZnCl_4]$.
7. What is the number of coordinate sites in
   a. EDTA?
   b. Ethylenediamine?
8. Arrange the following ligands in decreasing order of their power to cause the crystal field splitting. Give reasons.

$$F^-, Cl^-, Br^-, I^-$$

9. Explain why $[Co(NH_3)_6]^{3+}$ is orange whereas $[Co(H_2O)_6]^{3+}$ is blue in color.
10. What are the different factors affecting the stability of a complex?
11. Calculate the crystal field stabilization energy (CFSE) for the following complexes: $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$.
12. Explain why $[Co(NH_3)_6]^{3+}$ is diamagnetic whereas $[CoF_6]^{3-}$is paramagnetic even if both are octahedral complexes.
13. Distinguish between coordination number and oxidation number of the metal ion.
14. What is meant by the term ligand? Name one hexadentate ligand.
15. A coordination compound has the formula $CoCl_3{\cdot}4NH_3$. It does not liberate ammonia but precipitates silver ions as silver chloride. Write the structural formula and name of the complex.
16. What do crystal field stabilization energy and pairing energy mean?
17. What is the effect of the nature of ligand on the stability of the complex?
18. Give IUPAC names for the following complexes
   a. $[Co(NH_3)_3(NO_2)Cl(CN)]$
   b. $Na_3[Fe(CN)_5(CO)]$
   c. $[Co(en)_3]Cl_3$
19. Give the formula of each of the following complexes
   a. Potassiumtrioxalatoferrate(III)
   b. Sulphatopentam inecobalt(III) bromide
   c. *tetrakis*(ethylendiamine)μ-amido-μ-hydroxy-dicobalt(III) sulphate
   d. Tetrapyridineplatinum(II) tetrachoroplatinate(II)
20. What are chelating complexes?

Long–Answer Questions

1. Discuss the concept of primary and secondary valencies in coordination complex as postulated by Werner's coordination theory.
2. How does the formation of a coordination compound take place according to valence bond theory? What are the limitations of the theory?
3. Explain why $[Ni(CO)_4]$ is tetrahedral and $[Ni(NH_3)_6]^{2+}$ is octahedral using valence bond theory.
4. What are the salient features of crystal field theory?
5. Explain the crystal field splitting of *d*-orbitals by the ligands in octahedral complexes.
6. Both $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ are octahedral complexes. Use crystal field theory to predict the magnetic nature of the two complexes.

7. Apply crystal field theory to explain why
   - **a.** $Ti(H_2O)_6]^{3+}$ is colored and $[Sc(H_2O)_6]^{3+}$ is colorless.
   - **b.** $[Co(NH_3)_6]^{3+}$ is orange yellow in color and $[CoF_6]^{3-}$ is blue in color.
8. Show the splitting of *d*-orbitals of the central metal ion in $[Co(NH_3)_6]^{3+}$ ion. Arrange the electrons in the split *d*-orbitals and calculate the CFSE.
9. Draw and explain the splitting of 3*d*-orbitals in a tetrahedral ligand field. Why is Δ_t is approximately equal to $4/9\Delta_o$?
10. How do you differentiate the crystal field splitting of *d*-orbitals in an octahedral field from that in a tetrahedral field? Explain with a diagram.
11. If concentrated HCl or excess of KCl is added to an aqueous solution of $CoCl_2$, color changes from light pink to dark blue, but on dilution with water, the pink color is restored. Explain.
12. What value of magnetic moment would you expect in case of the following complexes?
   - **a.** $Ni(CO)_4$ **b.** $[CoF_6]^{3-}$
   - **c.** $[Fe\ (CN)_6]^{3-}$ **d.** $[Co(NH_3)_6]^{3+}$
13. Draw and explain the crystal field splitting of *d*-orbitals in the case of tetrahedral complexes. What are the factors affecting the value of splitting energy (Δ_t)?
14. Explain with diagram for the crystal field splitting of *d*-orbitals under the influence of octahedral ligand field. How low-spin and high-spin complexes are formed?

Answers

Multiple-Choice Questions

1. (b)
2. (c)
3. (d)
4. (b)
5. (d)
6. (a)

Fill in the Blanks

1. double salts, coordination compounds
2. coordination number
3. donor atom
4. *d*-orbitals
5. t_{2g}, e_g

5 Thermodynamics and Chemical Equilibrium

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Types of thermodynamic systems and processes.
- Energy of a thermodynamic system in terms of internal energy, heat and work.
- First law of thermodynamics, its mathematical expression and concept of enthalpy.
- Application of first law of thermodynamics to different types of processes in an ideal gas and to determine molar heat capacity, different thermochemical variables and bond energies.
- Limitations of the first law of thermodynamics and need for second law.
- Second law of thermodynamics and concept of entropy.
- Entropy changes in isolated system, ideal gas system and on mixing of ideal gases.
- Work function, free energy and their physical significance.
- Applications of Gibbs–Helmholtz equation.
- The chemical equilibrium.

Thermodynamics as the name suggests, is the study of flow of heat into or out of a system as it undergoes a physical or chemical transformation. Flow of heat, or any other form of energy, in turn, brings about changes in certain properties of the system, including temperature, pressure, volume and concentration of the system. The changes in these quantities from initial to final state of the system can be measured and they provide information regarding energy changes and accompanying changes in related quantities like heat and work.

The study of thermodynamics is based on three broad generalizations known as the first, second and third laws of thermodynamics. Based on these laws, thermodynamics helps us determine the quantitative relation between heat and other forms of energy; criteria for predicting the feasibilty of change (physical and chemical); extent of change before equilibrium is reached and efficiency of various types of engines. The study of thermodynamics however, has the following two limitations:

1. Thermodynamics only tells us about the initial and final states of the system. It is not concerned about the rate of the associated physical or chemical reaction.
2. Thermodynamics is applicable only to macroscopic systems and does not apply to microscopic systems of individual atoms or molecules.

5.1 Some Important Terms in Thermodynamics

Thermodynamic System

A thermodynamic system is any region of space which is under thermodynamic investigation, and the rest of the universe is the surroundings (Figure 1).

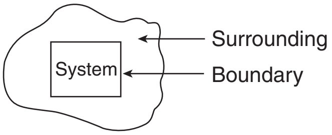


Figure 1 Schematic representation of thermodynamic system.

The real or imaginary surface separating the system from the surroundings is called boundary. In general, depending upon the nature of the boundary, thermodynamic systems can be of three types:

1. **Closed system:** In such a system, matter can neither be added nor removed, since the boundary of the system is sealed. The system is however, not insulated. In such a system, matter cannot be transferred but energy can be transformed in the form of heat or work to and from the surroundings {Figure 2(a)}. For example, gas contained in a cylinder fitted with a piston.
2. **Open system:** In such a system, matter can be added or removed from the system, since the boundary is open. The system is also not insulated. In such a system, both energy and matter can be transferred to and from the surroundings {Figure 2(b)}. For example, hot water tumbler placed on a table.
3. **Isolated system:** In such a system, neither energy nor matter can be transformed to or from the surroundings, since the boundary is both sealed and insulated. Such a system has no interaction with the surroundings {Figure 2(c)}. For example, boiling water contained in a thermal flask.

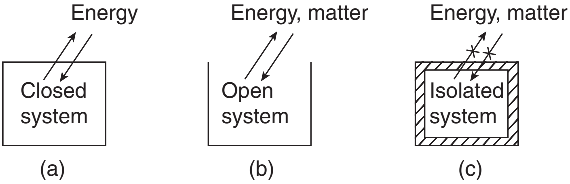


Figure 2 (a) Closed system; (b) open system and (c) isolated system.

Thermodynamic Processes

1. **Isothermal process:** It is a process carried out at constant temperature. For this process, the system is usually kept in contact with a constant temperature bath (thermostat) and the constant temperature is maintained by the exchange of heat with the thermostat.
2. **Adiabatic process:** It is a process in which heat cannot leave or enter the system. For this process, the system is thermally insulated from the surroundings. However, the temperature of the system may increase or decrease in an adiabatic process.
3. **Isobaric process:** It is a process carried out at constant pressure. All reactions carried out at atmospheric pressure are examples of isobaric process. However, volume change always takes place in an isobaric process.
4. **Isochoric process:** It is a process in which the volume of the system is kept constant ($dV = 0$). For example, heating of a substance in a non-expanding chamber.
5. **Cyclic process:** A process during which the system comes to its initial state through a number of different processes is called cyclic or cycle process. In this process change in internal energy and enthalpy is zero.

6. **Reversible process:** It is a process in which the energy change in each step of the process can be reversed in direction by making a small change in any property of the system, such as temperature, pressure, etc. Two important criteria for a process to be reversible are:
   - The change must be performed at an infinitesimal slow rate.
   - There must be no loss of energy due to friction and no finite temperature differences.
7. **Irreversible process:** It is a process in which the system or surroundings are not restored to their initial state at the end of the process. All processes occurring spontaneously in nature are irreversible. They always tend to proceed in a definite direction; and do not proceed in the opposite direction without the action of an external force. Irreversible processes take place spontaneously and not in infinitesimal slow steps that can be reversed. Some examples of irreversible process are expansion and diffusion of gases, flow of heat from a hotter body to a colder body, etc.

Thermodynamic Properties

1. **Intensive properties:** These are properties which are independent of the quantity of matter present in the system. For example, temperature, pressure, density, concentration, etc. If water in a glass (system under consideration) is divided into two equal or unequal parts, then both the parts will have same temperature, independent of the quantity of material present.
2. **Extensive properties:** These are properties that depend on the quantity of matter present in the system. For example, volume, number of moles, entropy, Gibb's free energy, enthalpy, etc. These properties are additive, while intensive properties are not.
3. **State of the system:** The set of variables, such as temperature, pressure, composition, etc., that describe the system is known as the state of the system. If any of these variables undergo a change, the system is said to undergo change of state.
4. **State function:** Any property of the system that depends on the state of the system, but is independent of the path that brings about that change in state is known as state function. For example, entropy, enthalpy, internal energy, Gibbs free energy, Helmholtz free energy, etc. are state functions. Work and heat are not state functions.
5. **Perfect differential:** If we have any single-valued variable (property) z, such that its value at any point of time is determined by any two variables (properties) x and y of the system at that point in a given state, then z is a perfect differential if:
   - The change $\mathrm{d}z$ between any two states is independent of the path by which the change is done, that is, it is a state function.
   - The value of $\mathrm{d}z$ for a cyclic process is zero.
   - The second differential of z with respect to x and y, carried out in any order is the same.

Energy of the Thermodynamic System

1. **Internal energy:** The total energy contained in a thermodynamic system is called **internal energy**. It includes all forms of kinetic as well as potential energy. Kinetic energy is associated with all kinds of motions, such as translational, rotational and vibrational, of particles of a system. Potential energy is associated with static energy of the particles. Hence, internal energy can mathematically be given as

$$E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{PE}}$$

   Internal energy is represented by E (or sometimes U). It is also called **intrinsic energy**. It depends on: (a) quantity of substance, (b) chemical nature of substance and (c) temperature, pressure, volume of the system. It is a state function, that is, its value depends on the state of the system and not on the path followed to obtain it. For example, the change in internal energy on heating one mole of water from 0°C to 100°C is 1.8 kcal. This value depends only on initial and final temperatures and not on how that temperature is attained.

Change in internal energy is denoted by ΔE, which depends on the initial and final energy values only, that is,

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

The SI unit of internal energy is joule (J). It can also be expressed in calories, where cal = 4.184 J.

2. **Heat:** The energy transferred because of temperature difference between two systems is called **heat**. It flows from system at higher temperature to the one at lower temperature. The amount of heat transferred (q) is proportional to the difference in temperatures:

$$q \propto \Delta T$$

or

$$q = C\Delta T$$

where C is the heat capacity of the system and is defined as the quantity of heat required to raise the temperature of a substance by 1°C. The quantity of heat is expressed in calories. Here, 1 cal is defined as the amount of heat required to raise the temperature of 1 g of water by 1°C at 15°C. By convention, when heat is absorbed by the system, q is positive and when heat is given out by the system, q is negative.

3. **Work:** It is the action/displacement of system against some force originating from the surroundings and acting on the boundary of the system. The energy of the system is its capacity to do work and the system may transfer energy to another system or surroundings through work. When work (W) is done by the system, its energy decreases; and when work is done on the system, its energy increases.

Work may also be in the form of expansion or compression of system known as the pressure–volume work. The volume change in expansion of solids and liquids is small, so the work done is small. However, in case of gases the volume change is substantial and work done by a gas in the system is equal to the change in volume against pressure p. (Note: Pressure can also be denoted by P. In this book it has been represented by p.)

$$W = p\Delta V$$

Concept Check

- What is the difference between a closed and an isolated system?
- What do you understand by the term state function?
- Differentiate between isochoric and isobaric processes.
- What is meant by the internal energy of the system?
- Heat and work are not state functions. Explain.

5.2 The First Law of Thermodynamics

The first law of thermodynamics is an application of the law of conservation of energy, which states that energy can neither be created nor destroyed, that is, the total energy of the system remains constant, though it may change from one form to another. Another statement for the first law arises from the fact that it is impossible to construct a perpetual motion machine (i.e., a machine which would produce work continously) that can produce work without consuming any energy.

Mathematical Expression for First Law of Thermodynamics

Let q be the amount of heat energy absorbed by the system. Some amount of absorbed heat energy is used by the system to perform work (W) and the rest is used to increase internal energy. The amount of work (W) is done by the system when its volume is increased from V_1 to V_2 at constant pressure (p) and is given by

$$W = p(V_2 - V_1) = p\Delta V$$

Again on absorption of heat the system increases its internal energy from E_1 to E_2. The increase in internal energy $\Delta E = E_2 - E_1$. Thus,

$$q = \Delta E + W$$

or

$$\Delta E = q - W \Rightarrow \Delta E = q - p\Delta V \tag{5.1}$$

Let the system release q amount of heat energy. It does so by decreasing its internal energy from E_2 to E_1 and by compressing its volume from V_2 to V_1 at constant pressure. The decrease in internal energy is given by $\Delta E = E_1 - E_2$. The compression at constant pressure takes place by the work done on the system and can be given by

$$p(V_1 - V_2) = -p\Delta V = -W$$

So,

$$q = \Delta E - W \Rightarrow \Delta E = q + W$$

For an infinitesimally small change dE in energy, the corresponding changes in heat and work are given by dq and dW and Eq. (5.1) can be written as:

$$\mathrm{d}E = \mathrm{d}q - \mathrm{d}W \tag{5.2}$$

Equations (5.1) and (5.2) are mathematical expressions for the first law of thermodynamics.

Interpretation of First Law of Thermodynamics

1. For a cyclic process, the values for initial and final internal energies are the same. Therefore,

   $$\Delta E = 0$$

   Using Eq. (5.1), we get

   $$q = W \tag{5.3}$$

   Thus for a cyclic transformation, the work done is equal to the heat absorbed or the net work done on the system, which is equal to the heat released by the system.
2. For an isochoric process, system volume remains constant, so dV = 0. Therefore, the pressure–volume work pdV is zero, that is,

   $$\mathrm{d}W = -p_{\text{ext}}\,\mathrm{d}V = 0$$

   Substituting in Eq. (5.2), we get

   $$\mathrm{d}E = \mathrm{d}q \tag{5.4}$$

Thus, for a system at constant volume, heat involved merely changes to internal energy. The heat absorbed is equal to increase in internal energy and heat evolved is equal to decrease in internal energy.

3. For an adiabatic process, no heat change is involved, therefore, $q = 0$. Substituting in Eq. (5.1), we get $\Delta E = W$. Thus, for an adiabatic process, the change in internal energy is equal to the work done on the system.
4. For an isobaric process, there is no change of pressure, thus the work done may be expressed as

$$W = p\Delta V$$

Substituting in Eq. (5.1), we get

$$\Delta E = q - p\Delta V \tag{5.5}$$

where

$$\Delta V = V_f - V_i$$

Problem 1

A system moves from state A to state B by a certain path, such that q and W are found to be + 160 cal and + 50 cal, respectively. Calculate ΔE of the system.

Solution

The first law of thermodynamics can be mathematically expressed as

$$\Delta E = q - W$$

Therefore, the change in internal energy can be calculated as

$$\Delta E = E_2 - E_1 = q - W = 160 - 50 = +110 \text{ cal}$$

Problem 2

Using first law of thermodynamics, show that heat is not a state function.

Solution

The essential criteria of a state function is that it must be a perfect differential. From the first law of thermodynamics, we have

$$\mathrm{d}E = \mathrm{d}q - \mathrm{d}W \tag{5.6}$$

Also, work done can be expressed in terms of pressure-volume work as

$$\mathrm{d}W = p\mathrm{d}V$$

Therefore,

$$\mathrm{d}q = \mathrm{d}E + p\mathrm{d}V \tag{5.7}$$

Taking E as a function of T and V, differential can be written as:

$$\mathrm{d}E = \left(\frac{\partial E}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial E}{\partial T}\right)_V \mathrm{d}T$$

Using this in Eq. (5.7), we get

$$\mathrm{d}q = \left(\frac{\partial E}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial E}{\partial T}\right)_V \mathrm{d}T + p\mathrm{d}V \tag{5.8}$$

At constant T, divide Eq. (5.8) by dV:

$$\left(\frac{\partial q}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T + p \tag{5.9}$$

Similarly at constant V, divide Eq. (5.8) by dT:

$$\left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{5.10}$$

Now, if heat (q) is a state function, then the following must be true from Euler's reciprocal relation:

$$\left(\frac{\partial^2 q}{\partial T \partial V}\right) = \left(\frac{\partial^2 q}{\partial V \partial T}\right) \tag{5.11}$$

Evaluating the second differentials of Eqs. (5.9) and (5.10), we get

$$\left(\frac{\partial^2 E}{\partial T \partial V}\right) + \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial^2 E}{\partial V \partial T}\right) \tag{5.12}$$

Since E is a state function, from Euler's relation we have

$$\left(\frac{\partial^2 E}{\partial T \partial V}\right) = \left(\frac{\partial^2 E}{\partial V \partial T}\right) \tag{5.13}$$

Using Eq. (5.13) in Eq. (5.12), we get

$$\left(\frac{\partial p}{\partial T}\right)_V = 0$$

This means that pressure is independent of temperature at constant volume. But this is contrary to Charles law, which states that at constant volume, the pressure of gas is directly proportional to its temperature in kelvin

$$\left(\frac{\partial p}{\partial T}\right)_V = T \neq 0$$

Hence, the assumption that q is a state function, is proven wrong and q is not a state function.

Concept Check

- State the first law of thermodynamics. How is it expressed mathematically?
- In a cyclic process, show that work done by the system is equal to the heat absorbed.
- Show that no external work is done when a system absorbs heat at constant volume.
- Using first law of thermodynamics, show that work is not a state function.

5.3 Enthalpy or Heat Content

Consider a change in the system from initial state (1) to the final state (2), carried out at constant pressure. The amount of heat absorbed during the process is q and the volume increases from V_1 to V_2. Then according to first law of thermodynamics, we have

$$\Delta E = q - W$$

or

$$q = \Delta E + W$$

Substituting $W = p\Delta V$, we get

$$q = (E_2 - E_1) + p(V_2 - V_1) \tag{5.14}$$

Equation (5.14) can be re-written as

$$q = (E_2 + pV_2) - (E_1 + pV_1)$$

The quantity $E + pV$ is known as **heat content** or **enthalpy** (H) of the system and ΔH is the enthalpy change for the process. Since E, p and V are state functions, H must also be a state function, that is, it does not depend on the path followed to reach the final state.

Change in enthalpy of a system from state 1 to state 2 can be expressed as

$$\Delta H = H_2 - H_1$$

Substituting values for initial and final states, we get

$$\begin{aligned}\Delta H &= (E_2 + p_2V_2) - (E_1 + p_1V_1)\\ &= (E_2 - E_1) + (p_2V_2 - p_1V_1)\end{aligned}$$

$$\Delta H = \Delta E + p\Delta V \tag{5.15}$$

or

$$\Delta H = \Delta E + W$$

According to first law of thermodynamics, $\Delta E = q - W$

or

$$q = \Delta E + W = \Delta E + p\Delta V \tag{5.16}$$

From Eqs. (5.15) and (5.16), we get that at constant pressure, $\Delta H = q$. It can also be written as

$$\Delta H = q_p$$

For solids and liquids, ΔV is very small; therefore, $p\Delta V$ is insignificant and $\Delta H = \Delta E$. For gases, ΔV and hence $p\Delta V$ have significant value, therefore at constant pressure, $\Delta H > \Delta E$.

For an ideal gas

$$pV = nRT$$

Let the gas undergo a change in volume from V_1 to V_2. So ideal gas equation can be written as:

$$pV_1 = n_1RT$$

$$pV_2 = n_2RT$$

Subtracting, we get

$$pV_2 - pV_1 = n_2RT - n_1RT \Rightarrow p\Delta V = \Delta nRT$$

where $\Delta n = (n_2 - n_1)$ = (number of moles of gaseous products − number of moles of gaseous reactants). Putting the value of $p\Delta V$ in Eq. 5.15, we get

$$\Delta H = \Delta E + \Delta nRT$$

Problem 3

Calculate the difference in ΔH and ΔE for combustion of methane at 25°C.

Solution

The combustion reaction of methane is given by

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The enthalpy change in the reaction is expressed as

$$\Delta H = \Delta E + \Delta nRT$$

Δn from the reaction is

$$\Delta n = 1 - (1 + 2) = -2$$

Therefore,

$$\Delta H = \Delta E - 2RT$$

Given that $T = 273 + 25 = 298$ K and $R = 1.985 \approx 2$ cal/K/mol. Substituting these, we calculate the difference in ΔH and ΔE as

$$\Delta H - \Delta E = -2 \times 2 \times 298 = -1192 \text{ cal}$$

Problem 4

For the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

at 25°C and 1 atm pressure, ΔH = –92.83 kJ/mol, calculate the change in internal energy.

Solution

For gaseous reactions,

$$\Delta H = \Delta E + \Delta nRT$$

so,

$$\Delta E = \Delta H - \Delta nRT$$

Given that $\Delta H = -92.83$ kJ/mol; Δn = stoichiometric coefficient of products – stoichiometric coefficient of reactants $= 2 - 4 = -2$; $R = 8.314 \times 10^{-3}$ kJ/mol/K and $T = 25 + 273 = 298$ K. Substituting these values in the above equation, we have

$$\Delta E = -92.83 - (-2) \times 8.314 \times 10^{-3} \times 298 = -92.83 + 4955.1 \times 10^{-3} = -92.83 + 4.955$$
$$= -87.875 \text{ kJ/mol}$$

Concept Check

- What is enthalpy of a system?
- What is the expression for enthalpy change for a system? Is it a state function?
- Show that (a) $\Delta H > \Delta E$ at constant pressure and (b) $\Delta H = \Delta E$ at constant volume.

5.4 Applications of First Law of Thermodynamics

Molar Heat Capacity

Heat capacity of a system refers to its capacity to absorb and store heat. It can be defined as the heat required to raise the temperature of a unit mass by 1°C (or K), at a specified temperature. Likewise, **molar heat capacity** is the amount of heat required to raise the temperature of one mole of the substance by 1°C (or K). It can be determined by rate of change of heat with temperature

$$C = \frac{dq}{dT}$$

From first law of thermodynamics,

$$dq = dE + p\,dV$$

Therefore,

$$C = \frac{dE + p\,dV}{dT}$$

Molar heat capacity can be determined at constant volume (C_V) and at constant pressure (C_p).

1. At constant volume, $dV = 0$, therefore C_V is given by

$$C_V = \frac{dE}{dT}$$

In terms of partial differentials, it is expressed as

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{5.17}$$

2. At constant pressure,

$$C_p = \frac{\mathrm{d}E}{\mathrm{d}T} + p\left[\frac{\mathrm{d}V}{\mathrm{d}T}\right]$$

In terms of partial differentials, it is expressed as

$$C_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

On differentiating the expression $H = E + PV$ with respect to temperature at constant pressure, it can be expressed as

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

On comparing with the preceding equation, we get

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{5.18}$$

Relation between C_p and C_V

By definition,

$$H = E + pV \tag{5.19}$$

At constant pressure,

$$\Delta H = \Delta E + p\Delta V \tag{5.20}$$

We know that H is a function of T and p, that is

$$H = f(T, p)$$

Differentiating Eq. (5.19) with respect to temperature at constant pressure, we get

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + p\frac{\partial V}{\partial T} + V\frac{\partial p}{\partial T} \tag{5.21}$$

At constant pressure,

$$\frac{\partial p}{\partial T} = 0$$

Therefore Eq. (5.21) becomes,

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + p\frac{\partial V}{\partial T} \tag{5.22}$$

For one mole of an ideal gas, $pV = RT$. Differentiating with respect to temperature, we get

$$\frac{\partial V}{\partial T} = \frac{R}{p} \tag{5.23}$$

Substituting Eq. (5.23) in Eq. (5.22), we get

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + R \tag{5.24}$$

We know that E is a function of T and V, that is

$$E = f(T, V)$$

Since dE is a complete differential, we can write as:

$$\partial E = \left(\frac{\partial E}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial E}{\partial V}\right)_T \mathrm{d}V$$

Differentiating the above equation w.r.t. temperature at constant pressure, we get

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{5.25}$$

Using the value of $\left(\frac{\partial E}{\partial T}\right)_p$ from Eq. (5.25), Eq. (5.24) can be rewritten as

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + R \tag{5.26}$$

We know that heat capacity at constant pressure

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

and heat capacity at constant volume

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

Substituting these values in Eq. (5.26), we get

$$C_p = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + R \tag{5.27}$$

where $\left(\frac{\partial E}{\partial V}\right)_T$ is called **internal pressure** and for an ideal gas it is zero. So,

$$C_p = C_V + R$$

or
$$C_p - C_V = R \tag{5.28}$$

where R is the universal gas constant. Equation (5.28) gives the relation between molar heat capacities at constant volume and pressure for an ideal gas. For solids and liquids, there is no volume change, so $\Delta V = 0$. Substituting in Eq. (5.20), we get

$$\Delta H = \Delta E$$

Therefore, $C_p = C_V$.

Reversible Isothermal Expansion/Compression of an Ideal Gas

In an isothermal process, temperature of the system remains constant, therefore, $\mathrm{d}E = 0$ or $\Delta E = 0$. Substituting in the equation for first law of thermodynamics, we get

$$\mathrm{d}E = \mathrm{d}q - \mathrm{d}W = 0$$

Therefore,
$$\mathrm{d}q = \mathrm{d}W$$

or
$$q = W \tag{5.29}$$

Hence, in an isothermal process, the expansion or compression of an ideal gas takes place at the expense of heat absorbed or given out. Similarly, the enthalpy change for an isothermal expansion is also zero as:

$$\begin{aligned}\Delta H &= \Delta E + \Delta(pV)\\ &= \Delta E + \Delta(nRT) \quad (\text{as } pV = nRT)\\ &= \Delta E + nR(\Delta T)\\ &= 0 + 0 = 0 \qquad (\text{as } \Delta E \text{ and } \Delta T = 0 \text{ for an isothermal process})\end{aligned}$$

For an isothermal expansion, the gas expands reversibly from volume V_1 to volume V_2 and correspondingly, the pressure decreases from p_1 to p_2. Thus the work done is given by

$$W = \int_{V_1}^{V_2} p\mathrm{d}V \tag{5.30}$$

From ideal gas equation, we have

$$pV = nRT$$

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

Substituting for p in Eq. (5.30), we get

$$W = \int_{V_1}^{V_2} \frac{nRT}{V}\mathrm{d}V = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{p_1}{p_2}$$

because at constant temperature

$$\frac{V_2}{V_1} = \frac{p_1}{p_2}$$

Work done can also be expressed as

$$W = 2.303nRT \log \frac{V_2}{V_1} \tag{5.31}$$

The work done under reversible conditions corresponds to W_{max}.

Adiabatic Expansion of an Ideal Gas

A perfectly insulated system is called an adiabatic system. In such system, no heat exchange takes place between the system and surroundings, therefore $q = 0$.

According to the first law of thermodynamics, $\Delta E = q - W$. For an adiabatic process,

$$\Delta E = -W \tag{5.32}$$

Thus for an adiabatic process, the work is done at the expense of internal energy. The decrease in internal energy during expansion, thereby causes a fall in temperature.

Consider one mol of an ideal gas at pressure p and volume V. The work done for an infinitesimal increase in volume $\mathrm{d}V$ at pressure p is given by $p\mathrm{d}V$. The decrease in internal energy $= \mathrm{d}E$. Therefore,

$$\mathrm{d}E = -\,p\mathrm{d}V \tag{5.33}$$

We know that,

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V$$

$$\mathrm{d}E = C_V\mathrm{d}T \tag{5.34}$$

Equating Eqs. (5.33) and (5.34), we get

$$C_V\mathrm{d}T = -p\mathrm{d}V \tag{5.35}$$

For an ideal gas,

$$p = \frac{RT}{V}$$

Substituting in Eq. (5.35), we get

$$C_V\mathrm{d}T = \frac{-RT}{V}\mathrm{d}V$$

or

$$C_V\frac{\mathrm{d}T}{T} = -R\frac{\mathrm{d}V}{V}$$

Integrating between the limits T_1, T_2, and V_1, V_2, we get

$$C_V \int_{T_1}^{T_2} \frac{\mathrm{d}T}{T} = -\mathrm{R} \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V}$$

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

Since $C_p - C_V = R$, we get

$$\ln \frac{T_2}{T_1} = -\frac{(C_p - C_V)}{C_V} \ln \frac{V_2}{V_1}$$

Also, ratio of molar heat capacities is given by

$$\gamma = \frac{C_p}{C_V}$$

Substituting, we get

$$\ln \frac{T_2}{T_1} = -(\gamma - 1) \ln \frac{V_2}{V_1}$$

taking antilogarithms

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \tag{5.36}$$

$$T_2 {V_2}^{\gamma - 1} = T_1 {V_1}^{\gamma - 1}$$

or

$$TV^{\gamma - 1} = \text{constant}$$

Also, by ideal gas equation

$$\frac{T_2}{T_1} = \frac{p_2 V_2}{p_1 V_1} = \left[\frac{V_1}{V_2} \right]^{\gamma - 1}$$

Equating Eqs. (5.36) and (5.37), we get

$$\frac{p_2}{p_1} = \left(\frac{V_1}{V_2} \right)^{\gamma}$$

$$p_1 {V_1}^{\gamma} = p_2 {V_2}^{\gamma} \tag{5.37}$$

or

$$pV^{\gamma} = \text{constant}$$

Problem 5

For one mole of an ideal gas, $T = f(p,V)$. Show that dT is a perfect differential.

Solution

$$T = f(p,V)$$

$$\mathrm{d}T = \left(\frac{\partial T}{\partial p}\right)_V \mathrm{d}p + \left(\frac{\partial T}{\partial V}\right)_p \mathrm{d}V$$

For an ideal gas, $pV = RT$

or $$T = \frac{pV}{R}$$

Differentiating with respect to pressure at constant volume, we get

$$\left(\frac{\partial T}{\partial p}\right)_V = \frac{V}{R} \tag{5.38}$$

Differentiating with respect to volume at constant pressure, we get

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{R} \tag{5.39}$$

Differentiating Eq. (5.38) with respect to volume, we get

$$\frac{\partial^2 T}{\partial V \cdot \partial p} = \frac{1}{R} \tag{5.40}$$

Differentiating Eq. (5.39) with respect to pressure, we get

$$\frac{\partial^2 T}{\partial p \cdot \partial V} = \frac{1}{R} \tag{5.41}$$

From Eqs. (5.40) and (5.41), we get

$$\frac{\partial^2 T}{\partial V \cdot \partial p} = \frac{\partial^2 T}{\partial p \cdot \partial V}$$

This shows that dT is a perfect differential.

Problem 6

Calculate the maximum work done when 0.5 mol of a gas expands isothermally and reversibly from a volume of 2 l to 5 l at 27°C. What is the change in internal energy if 200 cal of heat is absorbed?

Solution

For a reversible isothermal process, work done is given by

$$W = nRT \ln \frac{V_2}{V_1}$$

Given that $n = 0.5$ mol, $V_1 = 2$ l, $V_2 = 5$ l, $T = 273 + 27 = 300$ K and $R = 1.987$ cal/K/mol. Substituting these values in the equation, we get

$$\begin{aligned} W_{\text{max}} &= 0.5 \times 1.987 \times 300 \times \ln\left(\frac{5}{2}\right) \\ &= 0.5 \times 1.987 \times 300 \times 0.916 = 303.4 \text{ cal} \end{aligned}$$

According to first law of thermodynamics

$$q = \Delta E + W$$

Given that $q = 200$ cal. Substituting values of q and W in the above equation, we get

$$\Delta E = 200 - 303.4 = -103.4 \text{ cal}$$

Problem 7

Calculate the enthalpy change when 36 g of water is heated from 27°C to 37°C at 1 atm pressure. The molar heat capacity of water (18.1 cal/K/mol) remains constant in this temperature range.

Solution

Enthalpy change is given by

$$\Delta H = nC_p(T_2 - T_1)$$

Given that $C_p = 18.1$ cal/K/mol, $T_1 = 27 + 273 = 300$ K, $T_2 = 37 + 273 = 310$ K and $n = 36/18 = 2$ mol. Substituting values in the equation, we get

$$\Delta H = 2 \times 18.1 \times (310 - 300) = 36.2 \times 10 = 362 \text{ cal/mol}$$

Concept Check

- Define molar heat capacity. Give mathematical expression for heat capacity in terms of the first law of thermodynamics.
- Show that heat capacity at constant pressure is equal to rate of change of enthalpy with temperature.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

- For solids and liquids, $C_p = C_V$. Explain.
- Give the expression relating work done in a reversible isothermal expansion of an ideal gas to change in the volume of gas.

5.5 Thermochemistry

Thermochemistry is the study of energy or heat changes accompanying a chemical reaction or a physical change. A chemical reaction or physical transformation such as phase change is accompanied by evolution or absorption of heat. In other words, all physical or chemical changes cause conversion of chemical energy to heat energy or vice versa. Reactions which involve absorption of heat are called endothermic reactions, whereas reactions involving release of heat are called **exothermic reactions**.

Thermochemical Definitions

1. **Heat (enthalpy) of reaction:** It is the amount of heat absorbed or evolved in a particular reaction, when the number of moles of reactants as represented by the balanced chemical equation change completely into the products. It is the difference between the heat content or enthalpies of the products and the reactants. It is represented as

   $$\Delta H = \text{Heat of products} - \text{Heat of reactants.} = H_{\text{Products}} - H_{\text{Reactants}}$$

   The heat of reaction varies with the temperature. When heat of products is more than that of reactants, ΔH is positive. Heat will be absorbed during such a reaction, and the reaction will be endothermic. On the other hand if the heat of reactants is more than the heat of products, ΔH is negative. Heat will be evolved in such a reaction and the reaction will be exothermic.

   The heat change for a reaction taking place at 298 K and 1 atm is called **standard heat of reaction** or **standard enthalpy change** and is denoted by ΔH°. For example in the following reaction, $\Delta H^{\circ} = -284.5$ kJ.

   $$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

2. **Heat (enthalpy) of combustion:** It is the enthalpy change when one mole of the substance is completely burnt in excess of air. Since heat is always evolved during a combustion reaction, heat of combustion is always negative. For example, the enthalpy change involved in burning of carbon in presence of excess oxygen is given by $\Delta H = -94.05$ kcal.
3. **Heat (enthalpy) of neutralization:** It is the enthalpy change of a system when 1 g-equiv of an acid is neutralized by 1 g-equiv. of a base (or vice versa) in a dilute solution. For example, in the following neutralization reaction $\Delta H = -13.7$ kcal.

   $$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$$

   Enthalpy of neutralization of a strong acid and strong base is always −13.7 kcal, no matter which acid or base is employed. This is because it amounts to formation of water from its ions, and this value remains constant irrespective of the source of the ions.

   $$H^{+}(aq) + OH^{-}(aq) \rightarrow H_2O(l) \quad \Delta H = -13.7\text{ kcal}$$

4. **Heat (enthalpy) of formation:** It is the enthalpy change of a system when one mole of compound is formed from its constituent elements. It is represented as ΔH_f. For example, for the formation of iron sulphide from iron and sulphur, the heat of formation is $\Delta H_f = -24.0$ kcal.

   $$Fe(s) + S(s) \rightarrow FeS(s)$$

Standard heat of formation is the enthalpy change when one mole of a compound is formed from its constituent elements, at 298 K and one atmospheric pressure. It is represented as ΔH_f^o.

5. **Heat (enthalpy) of fusion:** It is the enthalpy change of the system when one mole of a solid substance is converted into the liquid state at its melting point. For example, when ice melts at 0°C, the heat of fusion is $\Delta H = +1.43$ kcal.

$$H_2O(s) \rightarrow H_2O(l)$$

6. **Heat (enthalpy) of vaporization:** It is the enthalpy change of the system when one mole of liquid is converted into vapor or gaseous state at its boiling point. For example, when water boils to form steam, the heat of vaporization is $\Delta H = +9.71$ kcal.

$$H_2O(l) \rightarrow H_2O(g)$$

7. **Heat (enthalpy) of sublimation:** It is the enthalpy change when one mole of a solid is directly converted into the gaseous form at a temperature below its melting point. For example, the heat of sublimation for iodine $\Delta H = +14.92$ kcal.

$$I_2(s) \rightarrow I_2(g)$$

Laws of Thermochemistry

Lavoisier–Laplace Law

It states that the enthalpy change accompanying a chemical process is same in magnitude but opposite in sign to the enthalpy change accompanying the same process in the reverse direction. This is also known as the first law of thermochemistry. For example, formation of water from its constituent elements is an exothermic process with $\Delta H = -286$ kJ/mol whereas decomposition of water into its constituent elements is an endothermic process with $\Delta H = +286$ kJ/mol.

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ/mol}$$

$$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g) \quad \Delta H = 286 \text{ kJ/mol}$$

Hess's Law of Constant Heat Summation

Since ΔE and ΔH are state functions, the heat liberated or absorbed in a given reaction must also be independent of the way in which the reaction is brought about, that means, it depends only on the initial and final states of the system and not on the path followed to achieve that state. This is postulated as the Hess's law, which states that

The heat absorbed or liberated in a given chemical equation is always constant and is the same whether the process occurs in one step or in several steps.

For example, we can verify Hess's law by considering the formation of CO_2 by the following two paths:

1. Burning of carbon in presence of oxygen can be carried out in a single step as:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -94.05 \text{ kcal}$$

2. The formation of CO_2 can take place through two steps:

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H = -26.42 \text{ kcal}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H = -67.71 \text{ kcal}$$

The overall reaction is:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -94.13 \text{ kcal}$$

The amount of heat liberated is about the same in both the cases.

Variation of the Heat of Reaction with Temperature (Kirchhoff's Equation)

We know that the heat of reaction varies with the temperature. Kirchhoff formulated mathematical expressions to relate the variation of heat of reaction with temperature, and this is known as **Kirchhoff's equation**. Using this relation we can find the enthalpy of a reaction at any temperature, if the value at some other temperature is given, along with the values of heat capacities for the reactants and products. For example, consider a reaction:

$$\mathrm{A + B \rightarrow C + D}$$

Enthalpy of the reaction is

$$\Delta H = (H_\mathrm{C} + H_\mathrm{D}) - (H_\mathrm{A} + H_\mathrm{B})$$

Rate of enthalpy change with temperature at constant pressure is given by

$$\left\{\frac{\partial(\Delta H)}{\partial T}\right\}_p = \left\{\left(\frac{\partial H_\mathrm{C}}{\partial T}\right)_p + \left(\frac{\partial H_\mathrm{D}}{\partial T}\right)_p\right\} - \left\{\left(\frac{\partial H_\mathrm{A}}{\partial T}\right)_p + \left(\frac{\partial H_\mathrm{B}}{\partial T}\right)_p\right\} \tag{5.42}$$

We know that

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

Substituting this in Eq. (5.42), we get

$$\left\{\frac{\partial(\Delta H)}{\partial T}\right\}_p = (C_{p,\mathrm{C}} + C_{p,\mathrm{D}}) - (C_{p,\mathrm{A}} + C_{p,\mathrm{B}}) = \Delta C_p$$

or

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}T} = \Delta C_p \tag{5.43}$$

Here ΔC_p is the difference in the heat capacities of products and reactants at constant pressure. Similarly, if the reaction is taking place at constant volume

$$\frac{\mathrm{d}\Delta E}{\mathrm{d}T} = \Delta C_V \tag{5.44}$$

Here ΔC_V is the difference in the heat capacities of products and reactants at constant volume. Equations (5.43) and (5.44) are known as **Kirchhoff's equations**. Rearranging Eq. (5.43), we get

$$\mathrm{d}(\Delta H) = \Delta C_p \, \mathrm{d}T$$

Integrating between the two values of enthalpy H_1 and H_2 at two different temperatures T_1 and T_2, we get

$$\int_{H_1}^{H_2} \mathrm{d}(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \mathrm{d}T$$

$$(\Delta H_2 - \Delta H_1) = \Delta C_p (T_2 - T_1) \tag{5.45}$$

Similarly,

$$(\Delta E_2 - \Delta E_1) = \Delta C_V (T_2 - T_1) \tag{5.46}$$

Bond Energy

Bond energy (B.E.) is the amount of energy required to break all the bonds present in one mole of a compound. Likewise, the energy liberated when a bond is formed between two atoms to form one mole of a compound is also called bond energy. It is also referred to as heat of formation of bond. In simpler words, bond energy measures the strength of the bond, that is, the force with which the atoms are bonded together. For example, bond energy of H−H bond is the energy needed to break all the bonds in one mole of hydrogen gas. It can be expressed in kcal/mol or kJ/mol.

Bond energy depends on many factors, such as electronegativity of the atoms, size of the atoms, bond length, etc. The chemical environment of the bond influences the bond energy. Bond breaking is an endothermic process, and is thus accompanied by absorption of energy. This leads to a positive value of bond energy. On the other hand, bond formation is an exothermic process, and is thus accompanied by a release of energy. This leads to a negative value of bond energy.

Applications of Bond Energy

1. **Determination of heat of reaction:** Bond energy is useful for calculating heats of reaction for gaseous reactions which involve substances having covalent bonds. For example, consider the formation of ethane from ethylene.

   $$\mathrm{H_2C = CH_2(g) + H_2(g) \rightarrow H_3C - CH_3}(g)$$

   In the reaction, 4C–H bonds of C_2H_4 remain unaffected. A double bond breaks in C_2H_4 and one H–H bond breaks in H_2. In terms of bond formation, one C–C and two C–H bonds are formed in ethane (C_2H_6).Therefore,

   $$\Delta H = -(\Delta H_{\mathrm{C-C}} + 2\Delta H_{\mathrm{C-H}}) - (\Delta H_{\mathrm{C=C}} + \Delta H_{\mathrm{H-H}})$$

   The heat of reaction can be calculated if the heats of formation or bond energy of C–C bond, C–H bond and bond dissociation energy for H–H bond, C=C bond are given.
2. **Determination of heat of formation:** The heat of formation or dissociation of a compound can be calculated from the bond energies of the constituent bonds. For example, consider the formation of ethane,

   $$\mathrm{2C(g) + 6H_2(g) \rightarrow 2C_2H_6(g)}$$

There are two C–C bonds and six C–H bonds. Therefore heat of formation can be expressed as

$$\Delta H_f = 2 \times \text{B.E.}_{C-C} + 6 \times \text{B.E.}_{C-H}$$

3. **Determination of resonance energy:** For a compound (like benzene) exhibiting resonance, there is a considerable difference between the enthalpy of formation or dissociation as calculated from bond energies and that determined experimentally. This difference arises due to stabilization by resonance and is a measure of the resonance energy. For example, consider the dissociation of benzene

$$C_6H_6(g) \rightarrow 6C(g) + 6H(g)$$

The calculated dissociation energy

$$\begin{aligned}\Delta H_d &= 3(\Delta H_{C-C}) + 3(\Delta H_{C=C}) + 6(\Delta H_{C-H}) \\ &= 3 \times 347.3 + 3 \times 615 + 6 \times 416.2 = 5384.1 \text{ kJ/mol}\end{aligned}$$

whereas, the experimental value is 5535.1 kJ/mol. The difference between the two values gives the resonance energy of benzene.

Problem 8

Calculate the heat of formation of HCl at 100°C given that standard heat of formation of HCl is −22060 cal and molar heat capacities of hydrogen, chlorine and hydrogen chloride are 6.82 cal/mol/deg, 7.71 cal/mol/deg and 6.81 cal/mol/deg; and these remain constant over the temperature range.

Solution

The reaction for formation of HCl from hydrogen and chlorine is given by

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 \rightarrow HCl$$

Given that $\Delta H_f^o = -22060$ cal, $T_1 = 25 + 273 = 298$ K, $T_2 = 100 + 273 = 373$ K, $C_{p(HCl)} =$ 6.81 cal/deg/mol; $C_{p(H_2)} = 7.71$ cal/deg/mol; $C_{p(Cl_2)} = 6.82$ cal/deg/mol. Therefore, ΔC_p can be calculated as

$$\begin{aligned}\Delta C_p &= C_{p(HCl)} - \frac{1}{2}C_{p(H_2)} - \frac{1}{2}C_{p(Cl_2)} \\ &= 6.81 - \frac{1}{2}(6.82) - \frac{1}{2}(7.71) = -0.455\end{aligned}$$

According to Kirchhoff's law,

$$\begin{aligned}\Delta H &= \Delta H_f^o + \Delta C_p(T_2 - T_1) = -22060 + (-0.455)\,(373 - 298) \\ &= -22060 + (-0.455) \times 75 = -22060 - 34.125 = -22094.125 \text{ cal}\end{aligned}$$

The heat of formation of HCl at 100°C is −22094.125 cal.

Problem 9

The combustion of butane is an exothermic process. ($\Delta H = -2878.7$ kJ/mol). Write a balanced equation for the reaction and calculate the standard enthalpy for formation of butane given that standard enthalpies for formation of CO_2 and H_2O are –393.5 kJ/mol and –285.8 kJ/mol, respectively. What is the value for ΔE° at 298 K?

Solution

The combustion of butane may be represented as:

$$C_4H_{10}(g) + 6.5O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \quad \Delta H = -\ 2878.7 \text{ kJ/mol}$$

The enthalpy change for the reaction is given by:

$$\Delta H^\circ = 4\Delta H_f^\circ\ (CO_2) + 5\Delta H_f^\circ (H_2O) - \{\Delta H_f^\circ (C_4H_{10}) + 6.5\Delta H_f^\circ (O_2)\}$$

Rearranging the equation, enthalpy for formation of butane is given by

$$\begin{aligned}\Delta H_f^\circ (C_4H_{10}) &= 4\Delta H_f^\circ (CO_2) + 5\Delta H_f^\circ (H_2O) - 6.5\Delta H_f^\circ (O_2) - \Delta H \\ &= 4\times(-393.5) + 5(-285.8) - 0 - (-2878.7) = -124.3 \text{ kJ/mol}\end{aligned}$$

Now, $\quad \Delta H = \Delta E + \Delta nRT$

or $\quad \Delta E = \Delta H - \Delta nRT$

For gaseous substances,

$$\Delta n = 4 - (1 + 6.5) = -3.5$$

$$R = 8.314\times10^{-3} \text{ kJ/K/mol}$$

$$T = 25 + 273 = 298 \text{ K}$$

Substituting these values in the equation, we get

$$\begin{aligned}\Delta E &= -2878.7 - (-3.5)\times 8.314\times10^{-3}\times 298 \\ &= -2878.7 + 8.671 = -2870.03 \text{ kJ/mol}\end{aligned}$$

Problem 10

Carbon dioxide can be removed from the atmosphere by reaction with barium oxide.

$$BaO(s) + CO_2(g) \rightarrow BaCO_3(s)$$

Compute the enthalpy change for the reaction using the following data

$$BaO(s) + 2HCl(g) \rightarrow BaCl_2(s) + H_2O(g) \quad \Delta H^\circ = -360 \text{ kJ}$$

$$BaCO_3(s) + 2HCl(g) \rightarrow BaCl_2(s) + H_2O(g) + CO_2(g) \quad \Delta H^\circ = -94 \text{ kJ}$$

Solution

Given that

$$BaO(s) + 2HCl(g) \rightarrow BaCl_2(s) + H_2O(g) \quad \Delta H^o = -360 \text{ kJ} \tag{5.47}$$

$$BaCl_2(s) + H_2O(g) + CO_2(g) \rightarrow BaCO_3(s) + 2HCl(g) \quad \Delta H^o = +94 \text{ kJ} \tag{5.48}$$

Adding Eqs. (5.47) and (5.48), we get

$$BaO(s) + 2HCl(g) + BaCl_2(s) + H_2O(g) + CO_2(g) \rightarrow BaCl_2(s) + H_2O(g) + BaCO_3(s) + 2HCl(g)$$

where $\Delta H^o = -266$ kJ. Cancelling like terms on both sides, we get

$$BaO(s) + CO_2(g) \rightarrow BaCO_3(s) \quad \Delta H = -266 \text{ kJ}$$

Therefore, the enthalpy change for the reaction is –266 kJ.

Concept Check

- What is the difference between heat of formation and heat of reaction?
- Hess's law is a consequence of law of conservation of energy. Explain.
- Show that Kirchhoff's equation can be used to calculate heat of reaction at any temperature, if heat of reaction at any other temperature and heat capacities of reactants and products are known.
- What do you understand from the terms bond energy and bond dissociation energy?

5.6 Joule–Thomson Effect

In an ideal gas, pV is constant at any given temperature at all pressures. When such a gas expands under adiabatic conditions in vacuum, no heat is evolved or absorbed and no external work or work to separate the molecules is done.

However, when real gases are allowed to expand into vacuum or low pressure region, the temperature of the gas is lowered. This effect was observed and investigated by James Prescott Joule and William Thomson, and is known as **Joule–Thomson effect**. The effect is attributed to the fact that work is done by the gas to overcome intermolecular force during expansion. This causes a decrease in internal energy, and hence a decrease in the temperature of the gas. This effect is important in liquefaction of gases.

In the experimental setup, an insulated tube (adiabatic conditions) was fitted with a porous plug to allow gases to be kept at different pressures on either side. Volume V_1 of the gas at pressure p_1 was allowed to pass through the porous plug to a region where constant pressure is p_2 and volume of the gas became V_2, using two frictionless pistons at the end of the tube.

From the above setup,

$$\text{Work done by the system} = p_1V_1$$
$$\text{Work done on the system} = p_2V_2$$

From first law of thermodynamics

$$\Delta E = q - W = -(p_2V_2 - p_1V_1) = p_1V_1 - p_2V_2 \quad (\text{as } q = 0)$$

or $$E_2 - E_1 = p_1V_1 - p_2V_2$$

or $$E_2 + p_2V_2 = E_1 + p_1V_1$$

or $$H_2 = H_1$$

Thus, the process is isoenthalpic or conducted at constant enthalpy. Under such conditions, James Prescott Joule and William Thomson observed that all gases, with the exception of hydrogen, experienced a cooling on expansion. Hydrogen was found to become warmer. The change in temperature was found to depend on initial temperature and pressure of gas. The rate of change of temperature with pressure at constant enthalpy is called Joule–Thomson coefficient and is denoted by μ.

$$\mu = \left(\frac{\partial T}{\partial p}\right)_{\mathrm{H}}$$

In this expansion process ∂p is negative because initial pressure is greater than the final pressure (i.e., pressure in vacuum). So,

1. μ is positive when ∂T is negative or when temperature falls and
2. μ is negative when gas becomes warmer on expansion.

A study of Joule–Thomson coefficient for a gas at various temperatures and pressures reveals that at any given temperature, μ decreases with increase in pressure and becomes negative when the pressure is increased to a high value. This suggests that gases cool on adiabatic expansion at lower pressure and undergo a heating effect at higher pressure.

The pressure at which gases neither cool nor warm up on expansion, that is, $\mu = 0$ is called the **inversion point**. This point varies with temperature and for a given pressure, the temperature at which a gas on passage from higher to lower pressure through fine orifice does not undergo heating or cooling ($\mu = 0$) is known as **inversion temperature**. At constant pressure, each gas shows two inversion temperatures, the upper and lower one, between which it undergoes cooling on expansion and beyond which it undergoes heating. Most of the gases are below their upper inversion temperature at room temperature and hence cool on expansion. Hydrogen on the other hand, at room temperature, is above the upper inversion temperature and heats up on expansion.

Concept Check

- Joule–Thomson effect is of practical importance in liquefaction of gases. Explain.
- What is Joule–Thomson coefficient and what is its significance?
- While most of the gases cool on expansion, hydrogen becomes warmer. Explain.

5.7 The Second Law of Thermodynamics

The limitations of the first law of thermodynamics are as follows:

1. The first law specifies that the energy of an isolated system is constant and that one form of energy can be converted into an equivalent amount of energy of another form. However, it does not indicate or predict the feasibility of the conversion of energy and extent of such an energy conversion.
2. It establishes the relation between internal energy and enthalpy. It also provides expressions for heat changes occurring at constant volume or pressure. However, it does not specify the direction of heat flow.
3. It establishes the relation between heat and work. It also indicates the possibility of complete conversion of heat into mechanical work. However, experience shows that heat cannot be completely converted into an equivalent amount of mechanical work without proceeding some changes elsewhere.

These limitations are overcome by the **second law of thermodynamics**, which determines the direction and the extent of a chemical change. The various statements for second law are as follows:

1. Heat cannot flow from a colder body to a hotter body without the use of an external energy.
2. It is impossible to convert heat completely into an equivalent amount of work without proceeding changes elsewhere.
3. According to Clausius's statement, it is impossible for a cyclic process to transfer heat from a system at a lower temperature to a system at higher temperature, without applying some work or without converting some work into heat.
4. Every perfect machine working reversibly between the same temperatures of source (hot reservoir) or sink (cold reservoir) has the same efficiency whatever be the nature of substance used. This statement is also called Carnot's theorem.
5. According to Lord Kelvin, it is impossible to take heat from a hot reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cold reservoir. This statement recognizes the fact that the heat engines can never be 100% efficient.

Concept Check

- What is the main limitation of first law of thermodynamics?
- What is the significance of the second law of thermodynamics?

5.8 Entropy

Until Clausius introduced the term **entropy** in 1854, it was believed that only exothermic changes resulting in a lowering of internal energy or enthalpy could occur spontaneously. If this were true, then the melting of ice (an endothermic reaction), and many other such examples which took place spontaneously cannot be explained. Thus a new driving force called entropy was introduced to explain such changes. It is represented by symbol *S*. Entropy of a system is a thermodynamic property that is a measure of randomness or disorder of molecules in a system. In the above example, melting of ice or evaporation of water leads to an increase in randomness or disorder of the system. The water molecules have greater freedom of movement as compared to ice and this increases further on formation of water vapor.

Entropy is a state function and so depends only on initial and final states of the system. Change in entropy from one state to another is represented by ΔS and is given by

$$\Delta S = S_{\text{final}} - S_{\text{intial}}$$

Entropy is expressed in Joule/kelvin/mole (J/K/mol). A small differential change in entropy is given by

$$\mathrm{d}S = \frac{\mathrm{d}q}{T}$$

where dq is the infinitesimal quantity of heat absorbed under reversible conditions at absolute temperature T. A finite change in entropy can be given by

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

When heat is absorbed, q is positive and ΔS is also positive indicating an increase in entropy of the system.

The second law of thermodynamics may be stated in terms of entropy as "*the change in entropy of an isolated system is always positive when it undergoes a spontaneous process*". Since all natural processes are spontaneous and irreversible, they are accompanied by a net increase in entropy. So the second law of thermodynamics was also stated by Clausius as "*the entropy of the universe tends always to a maximum*".

Entropy Change for Isolated System (System and Surroundings)

Consider an isolated system comprising a gas cylinder enclosed in a heat reservoir, adiabatically insulated from the surroundings. The substance undergoes isothermal and reversible expansion at constant temperature T by absorbing quantity of heat q_{rev} from the reservoir. The entropy change of the substance is given by

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

The reservoir loses a quantity of heat q and thus entropy change of the reservoir is given by

$$\Delta S_{\text{r}} = \frac{-q_{\text{rev}}}{T}$$

Total entropy change of isolated system

$$\Delta S_1 = \Delta S + \Delta S_{\text{r}} = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{rev}}}{T} = 0$$

Similarly on isothermal and reversible compression of gas, the quantity of that q_{rev} is given out by the gas and gained by the reservoir. The total entropy change of the system is

$$\Delta S_2 = \Delta S + \Delta S_{\text{r}} = -\frac{q_{\text{rev}}}{T} + \frac{q_{\text{rev}}}{T} = 0$$

For the complete isothermal and reversible cycle, entropy change is given by

$$\Delta S_{\text{rev}} = \Delta S_1 + \Delta S_2 = 0$$

Thus for all processes carried out under isothermal and reversible conditions in an isolated system, the total entropy change is zero.

For an irreversible process, the expansion of gas occurs by absorption of heat q at constant temperature T. The actual value of q for an irreversible process may vary from $q = 0$ to $q = q_{\text{rev}}$, therefore $q \leq q_{\text{rev}}$. The entropy change of substance is however given by

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

since entropy change by definition is the heat absorbed under reversible conditions divided by absolute temperature and not the actual heat absorbed. The reservoir loses q quantity of heat, which can take place irreversibly; therefore, entropy change of reservoir is given by

$$\Delta S_{\text{r}} = \frac{-q}{T}$$

The total entropy change for system is

$$\Delta S_1 = \Delta S + \Delta S_{\text{r}} = \frac{q_{\text{rev}}}{T} - \frac{q}{T}$$

As $q_{\text{rev}} > q$, therefore $\Delta S_1 > 0$. Thus for an irreversible process occurring isothermally in an isolated system, an increase in the total entropy of the system is observed. On compression of substance, entropy change is

$$\Delta S = -\frac{q_{\text{rev}}}{T}$$

Entropy change of reservoir is given by

$$\Delta S_{\text{r}} = \frac{q_{\text{rev}}}{T}$$

The total entropy change for isolated system is

$$\Delta S_2 = \Delta S + \Delta S_{\text{r}} = 0$$

For the complete isothermal and irreversible cycle, the entropy change is given by

$$\Delta S_{\text{irr}} = \Delta S_1 + \Delta S_2 = \Delta S_1 \quad (\text{as } \Delta S_2 = 0)$$

or

$$\Delta S_{\text{irr}} > 0 \quad (\text{as } \Delta S_1 > 0)$$

This increase in entropy observed in irreversible isothermal cycle is due to conversion of work to heat. Most of the spontaneous processes occurring in nature are irreversible, so there is always a net increase in the entropy of the universe.

Entropy Change for System Only (Ideal Gas)

For processes occurring in isolated system, entropy can either remain constant or increase. However, if we consider only the system and not the surroundings, the entropy change for process may be positive, negative or zero. In a reversible process, if the gas expands isothermally on absorption of heat dq_{rev}, the entropy change is given by

$$dS = \frac{dq_{\text{rev}}}{T}$$

and work done is given by pdV. According to first law of thermodynamics

$$dE = dq - W = TdS - pdV$$

$$dS = \frac{dE}{T} + \frac{pdV}{T}$$

The entropy of a pure substance is a state function and varies with any of the two variables from T, V and p. When volume and temperature are independent variables, the relation may be expressed as

$$dS = \frac{C_V}{T}dT + \left(\frac{\partial p}{\partial T}\right)_V dV \tag{5.49}$$

For an ideal gas, $pV = nRT$. On differentiation with respect to T at constant volume, we get

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

Substituting in Eq. (5.49)

$$dS = \frac{nC_V dT}{T} + \frac{nRdV}{V}$$

Integrating both sides, we get

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_V dT}{T} + \int_{V_1}^{V_2} \frac{nRdV}{V} = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} \tag{5.50}$$

Similarly when temperature and pressure are independent variables

$$dS = \frac{C_p}{T}dT - \left(\frac{\partial V}{\partial T}\right)_p dp \tag{5.51}$$

For ideal gas equation, $pV = nRT$; or, on differentiation

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$$

Substituting in Eq. (5.51) for n moles of gas, we get

$$dS = n\frac{C_p}{T}dT - \frac{nR}{p}dp$$

Integrating both sides, we get

$$\Delta S = \int_{T_1}^{T_2} n\frac{C_p}{T}dT - \int_{p_1}^{p_2} nR\frac{dp}{p} = nC_p \ln\frac{T_2}{T_1} - nR\ln\frac{p_2}{p_1} \tag{5.52}$$

Case I: For isothermal process $T_1 = T_2$, so $\ln\frac{T_2}{T_1} = 0$.

Therefore, $$\Delta S = R\ln\frac{V_2}{V_1} = -R\ln\frac{p_2}{p_1}$$

Case II: For isobaric process, $p_1 = p_2$, so $\ln\frac{p_2}{p_1} = 0$.

Therefore, $$\Delta S = C_V \ln\frac{T_2}{T_1}$$

Case III: For isochoric process, $V_1 = V_2$, so $\ln\frac{V_2}{V_1} = 0$.

Therefore, $$\Delta S = C_\mathrm{V} \ln\frac{T_2}{T_1}$$

Entropy of a Mixture of Ideal Gases

We know that

$$\mathrm{d}S = C_\mathrm{V}\frac{\mathrm{d}T}{T} + R\frac{\mathrm{d}V}{V}$$

On integration

$$S = C_\mathrm{V}\ln T + R\ln V + S_0 \qquad \text{(where } S_0 \text{ is integration constant)}$$

Using $R = C_p - C_V$ in the above equation, we get

$$\begin{aligned}
S &= C_V \ln T + C_p \ln V - C_V \ln V + S_0 \\
&= C_V \ln T + C_p \ln\frac{RT}{p} - C_V \ln\frac{RT}{p} + S_0 \\
&= C_V \ln T + C_p \ln RT - C_p \ln p - C_V \ln RT + C_V \ln p + S_0 \\
&= C_V \ln T + C_p \ln R + C_p \ln T - C_p \ln p - C_V \ln R - C_V \ln T + C_V \ln p + S_0 \\
&= (C_p - C_V)\ln R + C_p \ln T - (C_p - C_V)\ln p + S_0 \\
&= C_p \ln T - R\ln p + R\ln R + S_0 \\
&= C_p \ln T - R\ln p + S_0' \qquad (\text{Since } R\ln R \text{ is constant}, R\ln R + S_0 = \text{constant} = S_0')
\end{aligned}$$

or $$S = C_p \ln T - R\ln p + S_0'$$

Therefore, entropy of a system consisting of a mixture of gases is given by the sum of the individual entropies of each gas at respective pressure or concentration present in the mixture.

Let the $n_1, n_2, n_3, \ldots$ be the number of moles of the various gases present in the mixture and $p_1', p_2', p_3', \ldots$ be their partial pressures, then the entropy of the mixture is given by

$$S = n_1(C_p \ln T - R\ln p_1' + S_0') + n_2(C_p \ln T - R\ln p_2' + S_0') + \ldots$$

or $$S = \sum n(C_p \ln T - R\ln p' + S_0')$$

The partial pressure (p') of an ideal gas is given by

$$p' = xp$$

where p' is the partial pressure, x is the mole fraction and p is total pressure. Substituting for p' in the equation, we get

$$S = \sum n(C_p \ln T - R \ln p - R \ln x + S_0') \tag{5.53}$$

Equation (5.53) is known as entropy of a mixture of ideal gases.

Entropy of Mixing

Entropy of mixing is defined as the difference between the entropy of the mixture of gases and the sum of the entropies of the separate gases, each at a pressure p. Thus,

$$\Delta S_{\text{mix}} = \sum n(C_p \ln T - R \ln p - R \ln x + S_{\text{i}}) - \sum n(C_p \ln T - R \ln p)$$

$$= -R\sum n \ln x = -R(n_1 \ln x_1 + n_2 \ln x_2 + ...)$$

or

$$\Delta S_{\text{mix}} = -R\sum n_{\text{i}} \ln x_{\text{i}} \tag{5.54}$$

where n_{i} and x_{i} represents number of moles and the mole fraction, respectively of the mixture of gases. If n is total number of moles then

$$n = n_1 + n_2 + n_3 + \dots$$

or

$$\frac{n}{n} = \frac{n_1}{n} + \frac{n_2}{n} + \frac{n_3}{n} + ...$$

or

$$1 = x_1 + x_2 + x_3 + ... = \sum x_i$$

Therefore,

$$\Delta S = -R\sum x_i \ln x_i \tag{5.55}$$

Entropy of mixing (ΔS_{mix}) is always positive. It is because x_{i} is a fraction and hence ln x_{i} will be negative.

Entropy of Physical Changes

All physical changes are accompanied by a change in entropy and are defined as follows.

1. **Entropy of fusion:** It is the increase in entropy when a solid substance melts at its melting point. It is always a positive value because melting results in an increase in randomness. It is denoted by ΔS_{fusion} and is expressed as

   $$\Delta S_{\text{fusion}} = S_{\text{liquid}} - S_{\text{solid}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{m}}}$$

   where T_{m} is the melting point of the solid.
2. **Entropy of vaporization:** It is the increase in entropy when a liquid substance vaporizes at its boiling point. It is always a positive value because vaporization always results in an increase in randomness.

   It is denoted by ΔS_{vap} and expressed as

   $$\Delta S_{\text{vap}} = S_{\text{vapor}} - S_{\text{liquid}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}}$$

where T_b is the boiling point of the liquid.

3. **Entropy of sublimation:** It is the increase in entropy when a solid substance converts directly into vapor at any temperature, that is, sublimation of a solid takes place. It is always a positive quantity because sublimation results in increase in randomness. It is denoted by ΔS_{sub} and is expressed as

$$\Delta S_{sub} = S_{vapor} - S_{solid} = \frac{\Delta H_{sub}}{T}$$

Entropy of Chemical Changes

The entropy change accompanying a chemical reaction is given by the difference between the sum of entropies of all products and sum of entropies of all reactants. For any chemical reaction:

$$\mathrm{A + B \rightarrow C + D}$$

the entropy change is given by

$$\Delta S = (S_C + S_D) - (S_A + S_B)$$

where S_A, S_B, S_C, S_D are entropies of A, B, C and D, respectively. For any chemical reaction, the entropy change is given by

$$\Delta S = \sum S_{products} - \sum S_{reactants}$$

The entropy of a substance at 25°C (298 K) and 1 atm pressure is called the standard entropy of the substance and is represented as S^o. In a chemical reaction, if all the reactants and products are in standard state, then the entropy change for the reaction is said to be standard entropy change and is expressed as

$$\Delta S^o = \sum S^o_{products} - \sum S^o_{reactants}$$

Problem 11

Calculate the change in entropy when 5 moles of an ideal gas expands from a volume of 4 l to 40 l at 27°C.

Solution

We know entropy change for a system is given by

$$\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\frac{V_2}{V_1}$$

At constant temperature

$$\Delta S = nR\ln\frac{V_2}{V_1} = nR \times 2.303\log\frac{V_2}{V_1}$$

$$= 5 \times 1.987 \times 2.303 \times \log\frac{40}{4} = 22.89 \text{ cal/deg}$$

Problem 12

(a) Calculate the entropy of fusion of ice if its heat of fusion is 6.01 kJ/mol at 273 K.
(b) Calculate the increase in entropy when one mole of water evaporates at 100°C, given that the latent heat of vaporization is 540 cal/g at 100°C.

Solution

(a) Entropy change for a phase transition is given by

$$\Delta S = \frac{\Delta H}{T}$$

The phase transformation for fusion of ice may be represented as

$$H_2O(s) \rightarrow H_2O(l)$$

Given that $\Delta H_{\text{fusion}} = 6.01$ kJ/mol $= 6010$ J/mol and $T = 273$ K. Substituting these values in the above equation, we get

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T} = \frac{6010}{273} = 22.01 \text{ J/K/mol}$$

(b) Now, 1 mol of water = 18 g. Therefore, latent heat of vaporization is

$$q_{\text{rev}} = 540 \times 18 = 9720 \text{ cal/mol}$$

Therefore, the increase in entropy is calculated as

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{9720}{373} = 26.06 \text{ cal/mol/K}$$

Problem 13

Calculate the change in entropy when 2 mol of an ideal gas
(a) undergoes a change from –5°C temperature and 3 atm pressure to –10°C temperature and 1.5 atm pressure, given that $C_V = 1.5\,R$.
(b) expands isothermally to 5 times its initial volume.

Solution

(a) Entropy change for this process will be given by

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) - nR\ln\left(\frac{p_2}{p_1}\right)$$

Given that $n = 2$ mol, $T_1 = 273 - 5 = 268$ K, $T_2 = 273 - 10 = 263$ K, $p_1 = 3$ atm, $p_2 = 1.5$ atm and $C_V = 1.5R$. Also,

$$C_p = C_V + R = 1.5R + R = 2.5R$$

Substituting values in the equation, we get

$$\begin{aligned}\Delta S &= 2\times 2.5\times 8.314\ \ln\frac{263}{268} - 2\times 8.314\times \ln\frac{1.5}{3}\\ &= 41.57\times -0.01883 - 16.628\times -0.693\\ &= -0.783 - (-11.523) = 10.47\ \text{J/K/mol}\end{aligned}$$

(b) Entropy change for the process will be given by

$$\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\left(\frac{V_2}{V_1}\right)$$

Given that $n = 2$ mol, $T_1 = T_2$ in an isothermal process, $R = 8.314$ J/K/mol, $V_2 = 5V_1$. Substituting these values in the equation, we get

$$\begin{aligned}\Delta S &= 2\times C_V \times \ln\frac{T_1}{T_2} + 2\times 8.314\times \ln\frac{5V_1}{V_1}\\ &= 0 + 16.628\times 1.61 = 26.762\ \text{J/K/mol}\end{aligned}$$

Concept Check

- What is entropy? Is it an intensive or extensive property?
- How does entropy change in a reversible and an irreversible process?
- How entropy change for an ideal gas is expressed when pressure and temperature are independent variables of the system?
- The process of mixing two or more gases is accompanied by an increase in entropy. Explain.
- An irreversible isothermal process is accompanied by an increase in entropy. Explain.

5.9 Free Energy

Helmholtz Free Energy

Helmholtz free energy is a thermodynamic function defined to measure the useful work obtainable from a closed system. It is denoted as A and is defined as

$$A = E - TS \tag{5.56}$$

where E is the internal energy, S is entropy and T in temperature absolute scale.

Since E, T and S are state functions of the system, therefore A is also a state function. Using first and second laws of thermodynamics, we can show that the change (decrease) in Helmholtz free energy is equal to the maximum work obtainable when the system undergoes a change.

Consider a change from state 1 to 2 at constant temperature,

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

or

$$\Delta A = \Delta E - T\Delta S \tag{5.57}$$

Equation (5.57) relates the increase in the function (ΔA), with change in internal energy (ΔE) and entropy (ΔS) of the sytem.

For a change carried out reversibly at constant temperature T, heat absorbed by the system is q, therefore

$$\Delta S = \frac{q}{T} \quad \text{or} \quad T\Delta S = q$$

Substituting this value of $T\Delta S$ in Eq. (5.57), we obtain

$$\Delta A = \Delta E - q \tag{5.58}$$

From the first law of thermodynamics,

$$q = \Delta E + W$$

or

$$-W = \Delta E - q \tag{5.59}$$

Comparing Eq. (5.58) with Eq. (5.59), we get

$$-\Delta A = W$$

Here negative sign indicates decrease in Helmholtz free energy and W is the maximum work obtainable by reversible process. Thus, $-\Delta A$ is a measure of maximum work obtainable at constant temperature and pressure.

Gibbs Free Energy

Of the total amount of work available with the system ($W_{\max}$), a part of it is used for pressure–volume work ($p\Delta V$). Therefore, the net energy available for work will be given by

$$\text{Net energy} = W_{\max} - p\Delta V$$

Another state function, Gibbs free energy, commonly known as free energy was defined to explain the nature of maximum net energy available from the system for useful work. Gibbs free energy of a system is denoted by G and is related to entropy and enthalpy by the relation

$$G = H - TS \tag{5.60}$$

Consider a system undergoing change from state 1 to state 2 at constant temperature

$$\Delta G = G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \tag{5.61}$$

We know that at constant pressure,

$$\Delta H = \Delta E + p\Delta V$$

Substituting in Eq. (5.61), we get

$$\Delta G = \Delta E + p\Delta V - T\Delta S$$

or
$$\Delta G = \Delta E - T\Delta S + p\Delta V \tag{5.62}$$

Putting the value of $\Delta E - T\Delta S$ from Eq. (5.57) in Eq. (5.62), we get

$$\Delta G = \Delta A + p\Delta V$$

Again, we know that $\Delta A = - W_{\max}$, so

$$\Delta G = - W_{\max} + p\Delta V$$

or
$$-\Delta G = W_{\max} - p\Delta V \tag{5.63}$$

Here $-\Delta G$ represents decrease in free energy. Thus Eq. (5.63) can be represented as

$$\left[\text{Decrease in free energy}\right] = \left[\text{Maximum work obtainable}\right] - \begin{bmatrix}\text{Work done by expansion} \\ \text{under constant pressure } p\end{bmatrix}$$
$$= \text{Maximum useful (or non-mechanical) or Net work } (W_{\text{net}})$$

Thus, $-\Delta G$ is a measure of maximum useful work obtainable from the system at a constant temperature and pressure, except mechanical work ($p\Delta V$).

Physical Significance of Free Energy

From the first law of thermodynamics, the total heat energy supplied to the system changes the internal energy of the system, causes expansion of gas (pressure–volume work) and is converted into useful work. This is represented as:

$$q = \Delta E + W_{\text{pressure}-\text{volume work}} + W_{\text{useful work}} = \Delta E + p\Delta V + W_{\text{useful-work}}$$
$$q = \Delta H + W_{\text{useful-work}} \tag{5.64}$$

For a reversible change carried out at constant temperature,

$$\Delta S = \frac{q}{T}$$

or
$$q = T\Delta S \tag{5.65}$$

Using Eqs. (5.64) and (5.65), we get

$$T\Delta S = \Delta H + W_{\text{useful-work}}$$

or
$$\Delta H - T\Delta S = -W_{\text{useful-work}}$$

or
$$-(\Delta G)_{p,T} = W_{\text{useful-work}} \tag{5.66}$$

Equation (5.66) shows that the decrease in free energy during a thermodynamic process is equal to the useful work obtainable from the system.

The free energy change for a system when the process is carried out at 25°C (298 K) and 1 atm pressure is called standard free energy change (ΔG^{o}). Thus, if for a chemical reaction, reactants in their standard state are converted into products in their states, the standard free energy change is given by

$$\Delta G^{\mathrm{o}} = \sum G^{\mathrm{o}}_{\text{products}} - \sum G^{\mathrm{o}}_{\text{reactants}} \tag{5.67}$$

The standard free energy change for a reaction is related to the equilibrium constant of the reaction by the relation

$$\Delta G^{\circ} = -2.303RT \times \log K_{\text{eq}} \tag{5.68}$$

For an electrochemical reaction, like that taking place in cell, the standard free energy change is related to the cell potential by the relation

$$-\Delta G^{\circ} = W_{\text{useful-work}} = \text{Electrical work} = nFE^{\circ} \tag{5.69}$$

where n is the number of electrons involved in the cell reaction; E° is the standard potential of cell and F is quantity of electricity expressed in Faraday.

Application of Free Energy to Gases

We know that, $G = H - TS$ and $H = E + pV$. Substituting the value of H in the first expression, we get

$$G = E + pV - TS \tag{5.70}$$

Differentiating Eq. (5.70), we get

$$\mathrm{d}G = \mathrm{d}E + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T \tag{5.71}$$

We know from first law of thermodynamics that

$$\mathrm{d}q = \mathrm{d}E + p\mathrm{d}V$$

Also,

$$\mathrm{d}S = \frac{\mathrm{d}q}{T} \Rightarrow \mathrm{d}q = T\mathrm{d}S$$

Substituting these values in Eq. (5.71), we get

$$\mathrm{d}G = T\mathrm{d}S + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$$

or

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T \tag{5.72}$$

At constant temperature, $\mathrm{d}T = 0$, so Eq.(5.72) becomes

$$\mathrm{d}G = V\mathrm{d}p \tag{5.73}$$

or

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{5.74}$$

Equation (5.74) implies that an increase in pressure increases the free energy at constant temperature. The more the volume of the system, the greater is the increase in free energy for a given increase in pressure. Thus, for a gas, the free energy increases much more rapidly (because it has larger volume) with pressure, as compared to that of a liquid or a solid. At constant pressure, $\mathrm{d}p = 0$, so Eq. (5.72) becomes

$$\mathrm{d}G = -S\mathrm{d}T \tag{5.75}$$

or

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{5.76}$$

The negative sign in Eq. (5.76) indicates that the free energy decreases with increase of temperature at constant pressure. The rate is greater for gases which have larger values of entropies than that for liquids or solids.

Let the system undergo a change from initial state (G_1 and p_1) to final state (G_2, p_2), the change in free energy is obtained by integrating Eq. (5.73)

$$\int_{G_1}^{G_2} \mathrm{d}G = \int_{p_1}^{p_2} V\mathrm{d}p$$

or
$$\Delta G = G_2 - G_1 = \int_{p_1}^{p_2} V\mathrm{d}p \tag{5.77}$$

From ideal gas equation, $V = nRT/p$. Substituting for V in Eq. (5.77), we get

$$\Delta G = \int_{p_1}^{p_2} \frac{nRT}{p}\mathrm{d}p$$

Since n, R, T are constants, we have

$$\Delta G = nRT\int_{p_1}^{p_2} \frac{\mathrm{d}p}{p} = nRT \ln\frac{p_2}{p_1} \tag{5.78}$$

In terms of volume, using relation $p_1V_1 = p_2V_2$, we get

$$\Delta G = nRT \ln\frac{V_1}{V_2} \tag{5.79}$$

Differential form of Helmholtz Free Energy

We know that $A = E - TS$. Differentiating the equation we get

$$\mathrm{d}A = \mathrm{d}E - T\mathrm{d}S - S\mathrm{d}T$$

Using the relations $\mathrm{d}E = \mathrm{d}q - p\mathrm{d}V$ and $\mathrm{d}q = T\mathrm{d}S$, we get

$$\mathrm{d}A = \mathrm{d}q - p\mathrm{d}V - \mathrm{d}q - S\mathrm{d}T$$

or
$$\mathrm{d}A = -p\mathrm{d}V - S\mathrm{d}T \tag{5.80}$$

At constant temperature, $\mathrm{d}T = 0$, therefore Eq.(5.80) becomes

$$\mathrm{d}A = -p\mathrm{d}V$$

or
$$\left(\frac{\partial A}{\partial V}\right)_T = -p \tag{5.81}$$

At constant volume, $\mathrm{d}V = 0$, therefore Eq.(5.80) becomes

$$\mathrm{d}A = -S\mathrm{d}T$$

or
$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{5.82}$$

Concept of Spontaneity

Spontaneous processes are those which occur on their own accord. These do not necessarily take place instantaneously, but are favorable and feasible. All natural processes are spontaneous, for example, diffusion of gas from higher to lower pressure, neutralization of acid by base, etc.

The driving force that is responsible for spontaneity of process may be discussed in terms of enthalpy change (ΔH), entropy change (ΔS) or free energy charge (ΔG). Spontaneous processes have a tendency to proceed in the direction of lower enthalpy. As a result, majority of exothermic changes are spontaneous though there are endothermic processes which are also spontaneous.

For a change to be spontaneous, the final state should have greater randomness and hence greater entropy than the initial state. In case of an isolated system, total entropy change is considered which is the sum total of entropy of system and surroundings.

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

For spontaneous process, $\Delta S_{\text{total}} > 0$; for a reversible or equilibrium process, $\Delta S_{\text{total}} < 0$. The conditions for spontaneity may also be defined considering the system alone. For a system in thermal equilibrium with its surroundings or undergoing reversible change, $\Delta S = 0$. If the system undergoes an irreversible change, then in absence of any change in internal energy or volume, all spontaneous processes will result in increase in entropy.

For a system undergoing a spontaneous change at constant temperature and pressure, ΔG must be negative. Free energy change may be expressed in terms of enthalpy and entropy change as

$$\Delta G = \Delta H - T\Delta S$$

ΔG will be negative if

1. ΔH is negative and ΔS is positive.
2. Both ΔH and ΔS are positive, and the magnitude of $T\Delta S > \Delta H$.
3. Both ΔH and ΔS are negative and the magnitude of $\Delta H > T\Delta S$.

Gibbs–Helmholtz Equation

Free energy of a system is given by $G = H - TS$. It is a state function and has different values at different states. Let G_1 and G_2 be the free energies of initial and final states, then

$$G_1 = H_1 - TS_1$$

where H_1 and S_1 are the enthalpy and entropy of the initial state, respectively at constant temperature T. Similarly,

$$G_2 = H_2 - TS_2$$

where H_2 and S_2 are the enthalpy and entropy of the final state, respectively at constant temperature T. Change in free energy can be given by

$$\Delta G = G_2 - G_1$$

Therefore,
$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$$
$$= (H_2 - H_1) - T(S_2 - S_1)$$

or
$$\Delta G = \Delta H - T\Delta S$$

We know from Eq. (5.75) that at constant pressure,

$$\mathrm{d}G = -S\mathrm{d}T$$

Thus, the free energy at the initial and final states can be given by

$$\mathrm{d}G_1 = -S_1\mathrm{d}T \quad \text{and} \quad \mathrm{d}G_2 = -S_2\mathrm{d}T$$

So,

$$\left(\frac{\partial G_1}{\partial T}\right)_p = -S_1 \tag{5.83}$$

$$\left(\frac{\partial G_2}{\partial T}\right)_p = -S_2 \tag{5.84}$$

Subtracting Eq. (5.83) from Eq. (5.84), we get

$$\left(\frac{\partial G_2}{\partial T}\right)_p - \left(\frac{\partial G_1}{\partial T}\right)_p = -S_2 - (-S_1)$$

or
$$\frac{\partial}{\partial T}(G_2 - G_1)_p = S_1 - S_2$$

or
$$\left[\frac{\partial}{\partial T}(\Delta G)\right]_p = -\Delta S$$

or
$$\Delta S = -\left[\frac{\partial}{\partial T}(\Delta G)\right]_p$$

Putting the value of ΔS from Eq. (5.61), we get

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p \tag{5.85}$$

This is known as **Gibbs–Helmholtz equation** in terms of change in Gibbs free energy and enthalpy at constant pressure. This equation is applicable to processes occurring at constant pressure. The relation may be used to calculate ΔH and measure the tendency of reaction to proceed by measuring ΔS.

Again,
$$A = E - TS$$

where A is the work function or Helmholtz free energy, E is the internal energy and S is entropy. Differentiating, we get

$$\mathrm{d}A = \mathrm{d}E - T\mathrm{d}S - S\mathrm{d}T$$
$$= \mathrm{d}q_{\mathrm{rev}} - p\mathrm{d}V - T\frac{\mathrm{d}q_{\mathrm{rev}}}{T} - S\mathrm{d}T$$

or $$dA = -pdV - SdT$$

At constant volume (V), $dV = 0$.

$$dA = -SdT$$

or $$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{5.86}$$

Work function is a state function. So it has different values at initial and final states. Let A_1 and A_2 be the work functions at initial and final states, respectively. Equation (5.86) can be written as

$$\left(\frac{\partial A_1}{\partial T}\right)_V = -S_1 \tag{5.87}$$

$$\left(\frac{\partial A_2}{\partial T}\right)_V = -S_2 \tag{5.88}$$

Subtracting Eq. (5.87) from Eq. (5.88), we get

$$\left(\frac{\partial A_2}{\partial T}\right)_V - \left(\frac{\partial A_1}{\partial T}\right)_V = -S_2 + S_1 = S_1 - S_2 = -(S_2 - S_1)$$

or $$\left[\frac{\partial (A_2 - A_1)}{\partial T}\right]_V = -\Delta S$$

or $$\left[\frac{\partial (\Delta A)}{\partial T}\right]_V = -\Delta S \tag{5.89}$$

We have known from Eq. (5.57) that

$$\Delta A = \Delta E - T\Delta S$$

Substituting value of ΔS from Eq. (5.89), we get

$$\Delta A = \Delta E + T\left[\frac{\partial (\Delta A)}{\partial T}\right]_V \tag{5.90}$$

This equation is also called as **Gibbs–Helmholtz equation** in terms of change in work function and internal energy at constant volume.

Application of Gibbs–Helmholtz Equation

Gibbs–Helmholtz equation can be applied to know the relation between enthalpy of a cell reaction and electrical energy produced in an electrochemical cell. Let us consider an electrochemical cell, in which nFE_{cell} amount of electrical energy is produced where n is the number of electrons transferred during cell reaction, F is the quantity of electricity produced and E_{cell} is the EMF of the cell or cell potential. According to Gibbs and Helmholtz, the electrical energy produced in an electrochemical cell is equal to the decrease in free energy accompanying the cell reaction.

So, decrease in free energy $(-\Delta G) = nFE_{\text{cell}}$.
Putting the value of ΔG in Gibbs Helmholtz equation, we get

$$-nFE_{\text{cell}} = \Delta H + T\left[\frac{\partial(-nE_{\text{cell}}F)}{\partial T}\right]_p$$

or

$$nFE_{\text{cell}} = -\Delta H + nFT\left[\frac{\partial E_{\text{cell}}}{\partial T}\right]_p \tag{5.90}$$

Here $-\Delta H$ represents heat energy is evolved.
Equation (5.90) has following three significances.

Case I: If temperature coefficient $(\partial E_{\text{cell}}/\partial T)_p$ is zero, $nFE_{\text{cell}} = -\Delta H$. That means the amount of heat energy released in a chemical reaction is equal to the amount of electrical energy produced when the same reaction is carried out in an electrochemical cell. It is clear from above that the amount of electrical energy (nFE_{cell}) produced is equal to the quantity of heat evolved only when there is no change in the value of E_{cell} by the change of temperature at constant pressure {i.e. $(\partial E_{\text{cell}}/\partial T)_p = 0$}.
Case II: If $(\partial E/\partial T)_p$ is positive, $nFE_{\text{cell}} > -\Delta H$. It indicates that the amount of electrical energy produced in an electrochemical cell is greater than the enthalpy of the cell reaction. That means an additional quantity of heat is required to carry out the cell reaction when E_{cell} increases with rise of temperature at constant pressure {i.e. $(\partial E_{\text{cell}}/\partial T)_p > 0$}. An additional amount of heat is supplied to the cell or the cell utilizes its own internal energy by decreasing its temperature in this case.
Case III: If $(\partial E/\partial T)_p$ is negative, $nFE_{\text{cell}} < -\Delta H$. It indicates that the amount of electrical energy produced in an electrochemical cell is less than the enthalpy of the cell reaction. That means some amount of heat energy is evolved during the cell reaction or temperature of the cell increases, when E_{cell} decreases with rise of temperature at constant pressure {i.e. $(\partial E_{\text{cell}}/\partial T)_p < 0$}.

Problem 14

Calculate the free energy and entropy change per mole when liquid water boils at 1 atm, given that for water $\Delta H_{vap} = 2.0723$ *kJ/g.*

Solution

The enthalpy of vaporization with molecular weight of water = 18 amu is calculated as

$$\Delta H_{\text{vap}} = 2.0723 \times 18 = 37.30\,\text{kJ/mol}$$

The entropy change is

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T_1} = \frac{37.30}{373\text{ K}}\text{kJ/mol} = 0.1\text{ kJ/mol/K} = 100\text{ J/mol/K}$$

where T_{b} is the boiling point of water. The free energy change is

$$\Delta G = \Delta H - T\Delta S = 37.30\text{ kJ/mol} - 373\text{K} \times 0.1\text{ kJ/mol/K} = 37.30\text{ kJ/mol} - 37.30\text{ kJ/mol} = 0$$

Problem 15

Calculate the entropy and free energy for the vaporization of 2 moles of liquid benzene at its boiling point (T_b = 80.2°C), given the latent heat of vaporization is 101 cal/g and molecular weight of benzene = 78 amu (assume ideal gas behavior for benzene vapor).

Solution

The enthalpy of the reaction is calculated as

$$\Delta H = 2 \times 101 \times 78 = 15756 \text{ cal}$$

Therefore using the above value of ΔH, we can calculate ΔS and ΔG as follows:

$$\Delta S = \frac{\Delta H}{T} = \frac{15756}{353.2} = 44.60 \text{ cal/K}$$

$$\Delta G = \Delta H - T\Delta S = 15756 - 353.2 \times 44.60 = 0.252 \approx 0 \text{ cal}$$

Problem 16

Compute the free energy change when 2 moles of an ideal gas expands reversibly and isothermally at 27°C from an initial volume of 5 l to 100 l.

Solution

For isothermal and reversible change, the free energy is calculated as

$$\Delta G = 2.303 \times nRT \times \log \frac{V_1}{V_2} = 2.303 \times 2 \times 8.314 \times 300 \ \log \frac{1}{20}$$
$$= 2.303 \times 2 \times 8.314 \times 300 \times (-1.3010) = -11486.98 \text{ J} = -11.487 \text{ kJ}$$

Problem 17

Predict at what temperature would the following reaction be spontaneous, given that ΔH = 9.080 kJ/mol and ΔS = 0.0357 kJ/K/mol.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

Solution

At equilibrium $\Delta G = 0$, therefore the equation for free energy

$$\Delta G = \Delta H - T\Delta S$$

can be written as $\Delta H = T\Delta S \quad (\text{as } \Delta G = 0)$

Substituting the given values of $\Delta H = 9.080$ kJ/mol and $\Delta S = 0.0357$ kJ/K/mol, we get

$$T = \frac{9.08}{0.0357} = 254.34 \text{ K}$$

At $T < 254.34$ K, $T\Delta S < \Delta H$ and $\Delta G > 0$. So, the reaction will not be spontaneous.
At $T > 254.34$, $T\Delta S > \Delta H$ and $\Delta G < 0$. So, the reaction will be spontaneous at $T > 254.34$ K.

Problem 18

Gibbs free energy change for a reaction at 25°C and 35°C are –25.5 kcal and –28 kcal, respectively. Calculate ΔS and ΔH at 35°C.

Solution

According to Gibbs–Helmholtz equation,

$$\Delta S = \frac{\partial \Delta G}{\partial T} = \frac{\Delta G_2 - \Delta G_1}{T_2 - T_1}$$

Given that $T_1 = 25 + 273 = 298$ K, $T_2 = 35 + 273 = 308$ K, $\Delta G_{1(298\text{K})} = -25.5 \text{ kcal} = -25500$ cal and $\Delta G_{2(308\text{ K})} = -28 \text{ kcal} = -28000$ cal. Substituting in the equation, we get

$$\Delta S = \frac{-28000 - (-25500)}{308 - 298} = \frac{-2500}{10} = -250 \text{ cal/deg}$$

Free energy is related to enthalpy and entropy by the equation

$$\Delta H = \Delta G + T\Delta S$$

At $T = 25°\text{C} = 298$ K, the enthalpy is

$$\Delta H = -25500 + 298(-250) = -25500 + (-74500) = -100000 \text{ cal} = -100 \text{ kcal}$$

Concept Check

- What is the physical significance of thermodynamic function free energy?
- For an isothermal process at constant pressure $\Delta G = W_{\text{net}}$. Explain it using mathematical expressions for first and second laws of thermodynamics.
- State Gibbs–Helmholtz equation and its important applications.

5.10 Maxwell Relations

These are mathematical relationships between different thermodynamic properties of a system. These are derived from differential forms of fundamental thermodynamic expressions and are useful for interpreting physical properties (p, V, T) of the system. Different Maxwell relations and their derivations are given below.

1. **Show that $(\partial T/\partial V)_S = -(\partial p/\partial S)_V$, if $dE = TdS - pdV$**

   Derivation
   We know that $dE = TdS - pdV$.
   At constant volume, $dV = 0$, So, $dE = TdS$

   or
   $$\left(\frac{\partial E}{\partial S}\right)_V = T$$

   Differentiating the above expression with respect to volume (V) at constant entropy, we get
   $$\frac{\partial^2 E}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S \tag{5.91}$$

   Similarly at constant entropy, $dS = 0$ and hence $dE = -pdV$

   or
   $$\left(\frac{\partial E}{\partial V}\right)_S = -p$$

   Differentiating the above expression with respect to entropy at constant volume, we get
   $$\frac{\partial^2 E}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_V \tag{5.92}$$

   Comparing Eqs. (5.91) and (5.92), we get
   $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{5.93}$$

2. **Show that $(\partial T/\partial p)_S = (\partial V/\partial S)_p$, if $dH = TdS + Vdp$**

   Derivation
   We know that $dH = TdS + Vdp$.
   At constant pressure, $dp = 0$, so $dH = TdS$

   or
   $$\left(\frac{\partial H}{\partial S}\right)_p = T$$

   Differentiating above expression with respect to pressure at constant entropy, we get
   $$\frac{\partial^2 H}{\partial S \partial p} = \left(\frac{\partial T}{\partial p}\right)_S \tag{5.94}$$

   Again, at constant entropy, $dS = 0$, so $dH = Vdp$

or
$$\left(\frac{\partial H}{\partial p}\right)_S = V$$

Differentiating above expression with respect to entropy at constant pressure, we get

$$\frac{\partial^2 H}{\partial S \partial p} = \left(\frac{\partial V}{\partial S}\right)_p \tag{5.95}$$

Comparing Eqs. (5.94) and (5.95), we get

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{5.96}$$

3. **Show that $(\partial S/\partial V)_T = -(\partial p/\partial T)_V$, if $\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$.**

Derivation
We know that $\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$.
At constant volume, $\mathrm{d}V = 0$, so $\mathrm{d}A = -S\mathrm{d}T$

or
$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Differentiating above expression with respect to volume at constant temperature, we get

$$\frac{\partial^2 A}{\partial T \partial V} = -\left(\frac{\partial S}{\partial V}\right)_T \tag{5.97}$$

Again, at constant temperature, $\mathrm{d}T = 0$, so $\mathrm{d}A = -p\mathrm{d}V$

or
$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

Differentiating above expression with respect to temperature at constant volume, we get,

$$\frac{\partial^2 A}{\partial T \partial V} = -\left(\frac{\partial p}{\partial T}\right)_V \tag{5.98}$$

Comparing Eqs. (5.97) and (5.98), we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{5.99}$$

4. **Show that $(\partial S/\partial p)_T = -(\partial V/\partial T)_T$, if $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$.**

Derivation
We know that $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$.
At constant pressure, $\mathrm{d}p = 0$, so $\mathrm{d}G = -S\mathrm{d}T$

or
$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Differentiating above expression with respect to pressure at constant temperature, we get

$$\frac{\partial^2 G}{\partial T \partial p} = -\left(\frac{\partial S}{\partial p}\right)_T \tag{5.100}$$

Again, at constant temperature, dT = 0, so dG = Vdp

or
$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

Differentiating above expression with respect to temperature at constant pressure, we get

$$\frac{\partial^2 G}{\partial T \partial p} = \left(\frac{\partial V}{\partial T}\right)_p \tag{5.101}$$

Comparing Eqs. (5.100) and (5.101), we get

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

or
$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{5.102}$$

5. **Show that $(\partial E/\partial S)_V = -(\partial H/\partial S)_p$ if dE = TdS – pdV and dH = TdS + Vdp.**

Derivation

Given that dE = TdS – pdV.
At constant volume, dV = 0, so dE = TdS

or
$$\left(\frac{\partial E}{\partial S}\right)_V = T \tag{5.103}$$

Also given that dH = TdS + Vdp.
At constant pressure dp = 0, so dH = TdS

or
$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{5.104}$$

Comparing Eqs. (5.103) and (5.104), we get

$$\left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p \tag{5.105}$$

6. **Show that $(\partial E/\partial V)_S = -(\partial A/\partial V)_T$, if $dE = TdS - pdV$ and $dA = -SdT - pdV$.**

Derivation
Given that $dE = TdS - pdV$.
At constant entropy, $dS = 0$, so $dE = -pdV$

or
$$\left(\frac{\partial E}{\partial V}\right)_S = -p \tag{5.106}$$

Also given that $dA = -SdT - pdV$
At constant temperature, $dT = 0$, so $dA = -pdV$

or
$$\left(\frac{\partial A}{\partial V}\right)_T = -p \tag{5.107}$$

Comparing Eqs. (5.106) and (5.107), we get

$$\left(\frac{\partial E}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T \tag{5.108}$$

7. **Show that $(\partial H/\partial p)_S = -(\partial G/\partial p)_T$, if $dH = TdS + Vdp$ and $dG = -SdT + Vdp$.**

Derivation
Given that $dH = TdS + Vdp$.
At constant entropy, $dS = 0$, $dH = Vdp$

or
$$\left(\frac{\partial H}{\partial p}\right)_S = V \tag{5.109}$$

Also given that $dG = -SdT + Vdp$.
At constant temperature, $dT = 0$, so $dG = Vdp$

or
$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{5.110}$$

Comparing Eqs. (5.109) and (5.110), we get

$$\left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T \tag{5.111}$$

8. **Show that $(\partial A/\partial T)_V = -(\partial G/\partial T)_p$,, if $dA = -SdT - PdV$ and $dG = -SdT + Vdp$.**

Derivation
Given that $dA = -SdT - pdV$.
At constant volume, $dV = 0$, so $dA = -SdT$

or
$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{5.112}$$

Also given that d$G = -S$d$T + V$dp.
At constant pressure, d$P = 0$, so d$G = -S$dT

or
$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{5.113}$$

Comparing Eqs. (5.112) and (5.113), we get

$$\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_p \tag{5.114}$$

Problem 19

Show that $\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_p = -\frac{H}{T^2}$

Solution

We know that d$G = V$d$p - S$dT,
At constant pressure, d$p = 0$, so the above expression will be written as

$$\mathrm{d}G = -S\,\mathrm{d}T$$

or
$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{5.115}$$

Again we know that $G = H - TS$

$$G - H = -TS$$

$$\frac{G-H}{T} = -S \tag{5.116}$$

Comparing Eqs. (5.115) and (5.116), we get

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G}{T} - \frac{H}{T} \tag{5.117}$$

Multiplying $1/T$, in both the sides of Eq. (5.117), we get

$$\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p = \frac{G}{T^2} - \frac{H}{T^2} \tag{5.118}$$

Differentiating $\left[\frac{\partial(G/T)}{\partial T}\right]_p$, we get

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{1}{T}\right)$$

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} \tag{5.119}$$

Comparing Eqs. (5.118) and (5.119),

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2}$$

The Criterion for Spontaneity or Feasibility of Chemical Reactions

Case I: If net increase in entropy of system and surrounding takes place, the process will be feasible and irreversible. It can be given by following equation.

$$\mathrm{d}S_{\text{sys}} + \mathrm{d}S_{\text{surr}} > 0 \tag{5.120}$$

Case II: If there is no net change in entropy of system and surrounding, the process is said to be in equilibrium. It can be given by following equation.

$$\mathrm{d}S_{\text{sys}} + \mathrm{d}S_{\text{surr}} = 0 \tag{5.121}$$

Combining Eqs. (5.120) and (5.121), we can write

$$\mathrm{d}S_{\text{sys}} + \mathrm{d}S_{\text{surr}} \geq 0 \tag{5.122}$$

Equation (5.122) represents the criteria for a process.
Let the heat lost by the surrounding in an isothermal process be $\mathrm{d}q_{\text{rev}}$.
So $\mathrm{d}S_{\text{surr}}$ can be given as:

$$\mathrm{d}S_{\text{surr}} = -\frac{\mathrm{d}q_{\text{rev}}}{T}$$

or,

$$\mathrm{d}S_{\text{surr}} = -\frac{\mathrm{d}E + p\mathrm{d}V}{T} \tag{5.123}$$

[Since $\mathrm{d}q_{\text{rev}} = \mathrm{d}E + p\mathrm{d}V$]
Putting the value of $\mathrm{d}S_{\text{surr}}$ from Eq. (5.123) in Eq. (5.122), we get

$$\mathrm{d}S_{\text{sys}} - \frac{\mathrm{d}E}{T} - \frac{p\mathrm{d}V}{T} \geq 0$$

$$T\mathrm{d}S - \mathrm{d}E - p\mathrm{d}V \geq 0$$

$$T\mathrm{d}S \geq \mathrm{d}E + p\mathrm{d}V \tag{5.124}$$

Equation (5.124) is the basic equation and gives a number of criteria for predicting the feasibility of a process or a reaction.

Criterion I: In terms of change in entropy of a reaction.
Let the volume and internal energy in a process remain constant. So $dE = 0$ and $dV = 0$. Putting these values in Eq. (5.124), we get

$$TdS \geq 0$$

or
$$(dS)_{E,V} \geq 0 \tag{5.125}$$

Equation (5.125) represents the following:

1. A process or a reaction is said to be feasible or spontaneous, if change in entropy is greater than zero or positive at constant internal energy and at constant volume.
2. If change in entropy is zero or there is no change in entropy at constant internal energy and at constant volume, the process or the reaction is in equilibrium.
3. The process or reaction is not feasible when it is carried out with decrease in entropy ($dS < 0$) at constant internal energy and at constant volume.

Criterion II: In terms of change in internal energy of a reaction.
Let the volume and entropy in a process remain constant. So $dV = 0$ and $dS = 0$. Putting these values in Eq. (5.123), we get,

$$(dE)_{S,V} \leq 0 \tag{5.126}$$

Equation (5.126) represents the following:

1. A process or a reaction is said to be feasible or spontaneous, if change in internal energy is less than zero or negative at constant entropy and at constant volume.
2. If change in internal energy is zero or there is no change in internal energy at constant entropy and at constant volume, the process or the reaction is in equilibrium.
3. The process or reaction is not feasible when it is carried out with increase in internal energy ($dE > 0$) at constant entropy and at constant volume.

Criterion III: In terms of change in enthalpy.
We know that $H = E + pV$ where H = enthalpy and E = internal energy.
Differentiating above expression, we get

$$dH = dE + pdV + Vdp$$

$$dE + pdV = dH - Vdp \tag{5.127}$$

Putting the value of $dE + pdV$ from Eq. (5.127) in Eq. (5.124), we get

$$TdS \geq dH - Vdp \tag{5.128}$$

At constant entropy, $dS = 0$ and at constant pressure, $dp = 0$. So Eq. (5.121) becomes

$$(dH)_{S,P} \leq 0 \tag{5.129}$$

Equation (5.129) represents the following:

1. A process or a reaction is said to be feasible or spontaneous, if change in enthalpy is less than zero or negative at constant entropy and at constant pressure.

2. If change in enthalpy is zero or there is no change in enthalpy at constant entropy and at constant pressure, the process or the reaction is in equilibrium.
3. The process or reaction is not feasible when it is carried out with increase in enthalpy ($\mathrm{d}H > 0$) at constant entropy and at constant pressure.

Criterion IV: In terms of change in work function or Helmholtz free energy.
We know that $A = E - TS$, where A is the work function, E is internal energy and S is entropy.
Differentiating above expression, we get

$$\mathrm{d}A = \mathrm{d}E - T\mathrm{d}S - S\mathrm{d}T$$

$$T\mathrm{d}S = \mathrm{d}E - S\mathrm{d}T - \mathrm{d}A \tag{5.130}$$

Putting the value of $T\mathrm{d}S$ from Eq.(5.130) in Eq. (5.124), we get

$$\mathrm{d}E - S\mathrm{d}T - \mathrm{d}A \geq \mathrm{d}E + p\mathrm{d}V$$

$$S\mathrm{d}T + \mathrm{d}A \leq -p\mathrm{d}V \tag{5.131}$$

If volume and temperature remain constant, $\mathrm{d}V = 0$ and $\mathrm{d}T = 0$. So Eq. (5.131) can be written as

$$(\mathrm{d}A)_{V,T} \leq 0 \tag{5.132}$$

Equation (5.132) represents the following:

1. A process or a reaction is said to be feasible or spontaneous, if change in work function or Helmholtz free energy is less than zero or negative at constant volume and at constant temperature.
2. If change in work function or Helmholtz free energy is zero or there is no change in work function or Helmholtz free energy at constant volume and at constant temperature, the process or the reaction is in equilibrium.
3. The process or reaction is not feasible when it is carried out with increase in work function or Helmholtz free energy ($\mathrm{d}A > 0$) at constant volume and at constant temperature.

Criterion V: In terms of change in free energy or Gibbs free energy.
We know that $G = H - TS$ where G is the free energy, H is enthalpy and S is entropy.

Again, $$H = E + pV$$

So, $$G = E + pV - TS$$

Differentiating above expression, we get

$$\mathrm{d}G = \mathrm{d}E + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$$

or $$\mathrm{d}E + p\mathrm{d}V = \mathrm{d}G - V\mathrm{d}p + T\mathrm{d}S + S\mathrm{d}T \tag{5.133}$$

Putting the value of $\mathrm{d}E + p\mathrm{d}V$ from Eq. (5.133) in Eq. (5.124), we get

$$T\mathrm{d}S \geq \mathrm{d}G - V\mathrm{d}p + T\mathrm{d}S + S\mathrm{d}T$$

$$\mathrm{d}G - V\mathrm{d}p + S\mathrm{d}T \leq 0 \tag{5.134}$$

Let pressure and temperature remains constant, $\mathrm{d}p = 0$ and $\mathrm{d}T = 0$. So Eq. (5.134) becomes

$$(\mathrm{d}G)_{p,\,T} \leq 0 \tag{5.135}$$

Equation (5.135) represents the following:

1. A process or a reaction is said to be feasible or spontaneous, if change in free energy or Gibbs free energy is less than zero or negative at constant pressure and at constant temperature.
2. If change in free energy or Gibbs free energy is zero or there is no change in free energy or Gibbs free energy at constant pressure and at constant temperature, the process or the reaction is in equilibrium.
3. The process or reaction is not feasible when it is carried out with increase in free energy or Gibbs free energy ($dG > 0$) at constant pressure and at constant temperature.

   The criterion in terms of free energy change is the most useful criterion to decide the feasibility as most of the processes are carried out at constant pressure and temperature.

Concept Check

- Express the criteria for equilibrium in terms of work function.
- For a system in equilibrium at constant temperature and pressure, show that $\Delta G = 0$.
- Comment on the spontaneity of the processes for which (a) $\Delta H < 0$, $\Delta S > 0$ and (b) $\Delta H > 0$ $\Delta S > 0$.
- What is the criterion of spontaneity in terms of free energy change and entropy change?

5.11 Chemical Equilibrium

Consider the following reversible reaction which is carried out in a closed container:

$$\mathrm{A + B \rightleftharpoons C + D}$$

The system is said to be in **chemical equilibrium** when the rate of forward reaction is equal to the rate of backward reaction. The state of equilibrium is dynamic because two processes are occurring simultaneously, but at the same rate. Chemical equilibria can be classified into two groups – homogeneous and heterogeneous equilibria. A homogeneous equilibrium is established in a system where all reactants and products are in the same phase, such as in a system containing only gases or liquids or solids. A heterogonous equilibria is established in a system where the reactants and products are in more than one phase, such as between solid and liquid, liquid and gas, solid and gas, etc. Some examples of the two types of equilibria are as follows:

$$\mathrm{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$$

$$\mathrm{CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)}$$

$$\mathrm{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$$

$$\mathrm{CuO(s) + H_2(g) \rightleftharpoons Cu(s) + HO_2(g)}$$

The characteristic features of chemical equilibrium state are as follows:

1. It is established in a closed system.
2. It is dynamic in nature.
3. It can be attained either from the reactants or the products side.

4. It is not affected by the presence of a catalyst.
5. At equilibrium state the rate of forward and backward reactions is the same.
6. At equilibrium state the concentration of the reactants and products remains constant.

The Law of Mass Action

According to **law of mass action**, the rate of a reaction is proportional to the product of effective concentration of the reacting species, each raised to a power which is equal the corresponding stoichiometric number of the substance in the balanced chemical equation. For example, consider a general reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

The rate of forward reaction is $K_f[A]^a[B]^b$. The rate of backward reaction is $K_b[C]^c[D]^d$. Here K_f and K_b are rate constants for forward and backward reactions, respectively. We know that at equilibrium, the rate of forward reaction is equal to the rate of backward reaction, therefore,

$$K_f[A]^a[B]^b = K_b[C]^c[D]^d$$

or

$$\frac{K_f}{K_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

or,

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{5.136}$$

where $K_C = K_f/K_b$ and is called the **concentration equilibrium constant**. For any reaction, it is constant for a specific temperature. For gaseous reactions, the concentration or active masses in Eq. (5.136) can be replaced by partial pressures to give

$$K_p = \frac{[p_C]^c \times [p_D]^d}{[p_A]^a \times [p_B]^b} \tag{5.137}$$

where p_A, p_B, p_C and p_D the partial pressures of A, B, C and D, respectively and K_p is called pressure equilibrium constant. The two equilibrium constants can be related using the ideal gas equation as follows:

$$pV = nRT$$

or

$$p = \frac{n}{V} \times RT = CRT$$

as number of moles per unit volume is equal to concentration.
Substituting this value of p in Eq. (5.130), we get

$$K_p = \frac{[C_C RT]^c \times [C_D RT]^d}{[C_A RT]^a \times [C_B RT]^b} = \frac{C_C^c \times C_D^d}{C_A^a \times C_B^b} \times (RT)^{(c+d)-(a+b)}$$

where $(c + d) - (a + b) = \Delta n$, that is, number of gaseous moles of products − number of gaseous moles of reactants. Therefore,

$$K_p = K_C \times (RT)^{\Delta n} \tag{5.138}$$

From Eq. (5.138), we have the following observations:

1. When the number of moles of products is equal to that of the reactants, that is $\Delta n = 0$; $K_p = K_C$.
2. When the number of moles of products is more than that of the reactants that is $\Delta n > 0$; $K_p > K_C$.
3. When the number of moles of products is less than that of reactants, that is, $\Delta n < 0$, $K_p < K_C$.

The value of equilibrium constant depicts the following characteristic features:

1. It is constant for a reaction at a given temperature and varies with change in temperature. For an endothermic reaction, it increases as the temperature is increased; and for an exothermic reaction it decreases as the temperature is increased.
2. It is independent of the original concentration of reactants and presence of the catalyst.
3. It is independent of the direction from which equilibrium is attained and the nature and number of steps involved in the reaction.
4. When it is large, the equilibrium of the reaction lies towards the products side.
5. For the reverse reaction, it is equal to the inverse of value for the forward reaction.

Units of K_p and K_C

Concentration is generally expressed in moles per liter and pressure in atmospheres. The units of K_p and K_C depend on the stoichiometry of the reaction. Consider the following cases:

Case 1: When total number of moles of reactants and products are equal. For example,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Here

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(\text{mol/l})^2}{(\text{mol/l})(\text{mol/l})} \Rightarrow \text{No units}$$

$$K_p = \frac{[p_{HI}]^2}{p_{H_2} p_{I_2}} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})} \Rightarrow \text{No units}$$

Thus, for such reactions, no unit is assigned to K_C and K_p.

Case 2: When the total number of moles of reactants and products are unequal. For example,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(\text{mol/l})^2}{(\text{mol/l})} = \text{mol/l}$$

$$K_p = \frac{[p_{NO_2}]^2}{p_{N_2O_4}} = \frac{(\text{atm})^2}{(\text{atm})} = \text{atm}$$

In such reactions, K_C will have units $(\text{mol/l})^{\Delta n}$ and K_p will have the units $(\text{atm})^{\Delta n}$; where Δn = total number of moles of products − total number of moles of reactants.

The Le Chatelier Principle

Le Chatelier principle states that if a system under equilibrium is subjected to a change, the system reacts in such a way so as to oppose the applied change, that is, the system tends to counteract the effects of any imposed stress. For example, when the temperature of a system in equilibrium is raised, the equilibrium shifts in such a manner that causes absorption of heat. The various changes that a system in equilibrium may undergo and their effects are discussed as follows:

1. **Change of concentration of a reactant or product:** When the concentration of a reactant is increased or that of a product is decreased, the equilibrium shifts towards the forward direction. Similarly, a decrease in the concentration of any reactant shifts the equilibrium in the backward direction.
2. **Change of pressure:** In case of gaseous reactions, an increase in pressure shifts the equilibrium in the direction where number of moles decreases. For example, in the formation of ammonia by Haber process

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22.0\,\text{kcal}$$

   The increase in pressure shifts the equilibrium in the forward reaction.
3. **Change of temperature:** An increase in temperature favors the forward reaction in case of an endothermic process and the backward reaction in an exothermic process. For example, in formation of ammonia (exothermic process) low temperature favors the forward reaction and high temperature favors the backward reaction.

   With the help of Le Chatelier principle, optimum conditions for securing the maximum yield of industrial process can be found out. For example, we have seen the effect of change of temperature and pressure on Haber process for manufacture of ammonia. Similarly, for manufacture of sulphuric acid by contact process, the conditions for maximum yield of sulphur trioxide may be fixed as follows:

$$2SO_2 + O_2 \rightleftharpoons SO_3 + 45\ \text{kcal}$$

   The forward reaction for the yield of sulphur trioxide will be favored by increase in concentration of SO_2 and O_2. High pressure and low temperature will also shift the equilibrium in the forward reaction. Optimum temperature and pressure conditions may thus be fixed to obtain maximum yield at effective cost using Le Chatelier principle.

Problem 20

The equilibrium constant K_C for the following reaction is 0.5 l^2/mol^2 at 400 K

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Find K_p, given that $R = 0.082$ l atm/deg/mol.

Solution

The given equilibrium is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Here $\Delta n = 2 - (1 + 3) = -2$. Substituting the values of Δn, K_C, R and T we get K_p as

$$K_p = K_C(RT)^{\Delta n} = 0.5 \times (0.082 \times 400)^{-2} = 4.636 \times 10^{-4}\,\text{atm}^2$$

Problem 21

A mixture containing 8.07 moles of hydrogen and 9.08 moles of iodine was heated at 448°C till equilibrium was attained when 13.38 mol of hydrogen iodide was obtained. Calculate the degree of dissociation of hydrogen iodide at 448°C.

Solution

The reaction of formation of HI is as follows:

$$\begin{array}{ccccc} H_2 & + & I_2 & \rightleftharpoons & 2HI \\ 8.07 & & 9.08 & & 0 \\ 8.07-x & & 9.08-x & & 2x \end{array}$$

Therefore, from the above data x can be calculated as

$$2x = 13.38 \Rightarrow x = \frac{13.38}{2} = 6.69$$

The equilibrium constant can be calculated as

$$K_C' = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(9.08-x)(8.07-x)}$$

$$= \frac{(13.38)^2}{(9.08-6.69)\times(8.07-6.69)} = 54.279$$

To calculate the dissociation constant of HI, consider the following reaction

$$\begin{array}{ccccc} 2HI & \rightleftharpoons & H_2 & + & I_2 \\ 0 & & 0 & & 0 \\ 1-2x & & x & & x \end{array}$$

From the above data, the dissociation constant is given by

$$K_C = \frac{x \times x}{(1-2x)^2} = \frac{x^2}{(1-2x)^2}$$

But

$$K_C = \frac{1}{K_C'} = \frac{1}{54.279} = 0.01842$$

Therefore x can be calculated as

$$\left(\frac{x}{1-2x}\right)^2 = \frac{1}{54.279}$$

$$\frac{x}{1-2x} = \sqrt{\frac{1}{54.279}}$$

$$\frac{x}{1-2x} = \frac{1}{7.3674}$$

or $$7.3674x = 1 - 2x$$

Therefore,

$$x = \frac{1}{9.3674} = 106.75 \times 10^{-3} \text{ mol}$$

$$\alpha = 2x = 2 \times 106.75 \times 10^{-3} = 213.5 \times 10^{-3}$$

or $$\text{Percentage dissociation} = 21.35$$

Chemical Potential of Multicomponent System

In a multicomponent system, change in free energy ($\mathrm{d}G$) at constant temperature and pressure may be expressed in terms of partial molar free energy ($\overline{G}_i$) and number of moles of component n as

$$(\mathrm{d}G)_{T,p} = \sum_i \overline{G}_i \mathrm{d}n_i \quad (i = \text{number of constituents})$$

When temperature and pressure are not constant, free energy change is given by

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_i \overline{G}_i \mathrm{d}n_i$$

The partial molar free energy was also called chemical potential by Gibbs and represented as μ, therefore, free energy change is

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

When a small amount of substance $i(\mathrm{d}n_i)$ is added to the system, keeping other variables constant, the change in free energy with change in composition is given by

$$(\mathrm{d}G)_{T,p} = \sum_i \mu_i \mathrm{d}n_i$$

This is known as Gibbs–Duhem equation. It gives the contribution of chemical potential of each component of the mixture per mole to the total free energy of the system at constant temperature and pressure.

The variation of chemical potential of component i of a multicomponent system, as a function of temperature is related to partial molar entropy of the component by the expression

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n_i} = -\overline{S}_i$$

Similarly, the variation of chemical potential of the component i of a multicomponent system, as a function of pressure is related to partial molar volume of the component by the expression

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i} = -\overline{V}_i$$

Van't Hoff Reaction Isotherm and Equations

Consider the following reaction in equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

The thermodynamic properties can be expressed in terms of partial molar free energies or chemical potential. For non-ideal system, free energy can be expressed in terms of activity as

$$G = G^{o} + RT \ln a$$

Therefore, chemical potential of any component may be expressed in terms of activity as

$$\mu = \mu^{o} + RT \ln a$$

In the above system at equilibrium, if the concentration of A and B diminishes by $a\mathrm{d}n$ and $b\mathrm{d}n$ moles, then there is a corresponding increase in concentrations of C and D by cdn and ddn moles. The free energy change can be expressed in terms of chemical potential as

$$(\mathrm{d}G)_{T,p} = \sum \mu_i \mathrm{d}n_i = (\mu_C c\mathrm{d}n + \mu_D d\mathrm{d}n) - (\mu_A a\mathrm{d}n + \mu_B b\mathrm{d}n)$$

or $$\Delta G = \left[c(\mu_C^o + RT \ln a_C) + d(\mu_D^o + RT \ln a_D)\right] - \left[a(\mu_A^o + RT \ln a_A) + b(\mu_B^o + RT \ln a_B)\right]$$

$$\Delta G = [(c\mu_C^o + d\mu_D^o) - (a\mu_A^o + b\mu_B^o)] + RT \ln\left[\frac{a_C^c a_D^d}{a_A^a a_B^b}\right]$$

$$0 = \Delta G^o + RT \ln\left[\frac{a_C^c a_D^d}{a_A^a a_B^b}\right] \quad (\text{as } \Delta G = 0 \text{ at equilibrium})$$

or $$-\left(\frac{\Delta G^o}{RT}\right) = \ln\left[\frac{a_C^c a_D^d}{a_A^a a_B^b}\right]$$

therefore, $$\Delta G^o = -RT \ln K$$

where K is called thermodynamic equilibrium constant and it is the ratio of the activities of products to those of reactants at equilibrium. The free energy change of reaction at any state is given by

$$\Delta G = \Delta G^o + RT \ln Q = -RT \ln K + RT \ln Q = RT \ln \frac{Q}{K}$$

where Q is the reaction quotient and is the ratio of activities of reactants and products at any state of reaction. The relation is known as **Van't Hoff reaction isotherm**. It is useful for determining the feasibility of a reaction under a given set of conditions. The variation in equilibrium constant K with temperature is given by Van't Hoff equation

$$\Delta G^o = -RT \ln K$$

or $$\ln K = -\frac{\Delta G^o}{RT}$$

Differentiating with respect to T, we get

$$\begin{aligned}\frac{\partial \ln K}{\partial T} &= -\frac{1}{R}\left(\frac{\partial(\Delta G^{\circ}/T)}{\partial T}\right)\\ &= -\frac{1}{R}\left(\frac{-\Delta H^{\circ}}{T^2}\right) \quad \text{(by Gibbs–Helmholtz equation)}\\ &= \frac{\Delta H}{RT^2} \quad \text{(as } \Delta H \text{ does not vary much with pressure, } \Delta H^{\circ} = \Delta H\text{)}\end{aligned}$$

This equation is known as Van't Hoff equation. Integrating this equation, we get

$$\ln k = \frac{-\Delta H}{RT} + \text{Constant}$$

or

$$\log k = \frac{-\Delta H}{2.303RT} + \text{Constant}$$

If integration is carried out between the temperatures T_1 and T_2, we get another useful form of Van't Hoff equation

$$\log\left(\frac{k_2}{k_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Problem 22

The standard free energy change for a reaction is $\Delta G^{\circ} = -41.8$ kJ/mol at 700 K and 1 atm. Calculate the equilibrium constant of the reaction at 700 K.

Solution

The standard free energy and equilibrium constant are related by the equation:

$$\Delta G^{\circ} = -RT \ln K = -2.303\,RT \log K$$

Given that $\Delta G^{\circ} = -41.8$ kJ $= -41800$ J, $T = 700$ K and $R = 8.314$ J/K/mol. Substituting these values in the equation, we get

$$-41800 = -2.303 \times 8.314 \times 700 \log K$$

$$-41800 = -13403 \log K$$

$$\log K = \frac{41800}{13403} = 3.1187$$

$$K = 1.312 \times 10^4$$

Concept Check

- How will you deduce the expression for equilibrium constant by applying law of mass action?
- How is the pressure equilibrium constant related to concentration equilibrium constant?
- Using Le Chatelier's principle, suggest the conditions under which high yield of ammonia may be obtained using Haber's process.
- For the reaction

  $$H_2 + I_2(g) \rightleftharpoons 2HI(g)$$

  What is the effect of
  a. addition of more hydrogen gas?
  b. removal of HI from the mixture?
  c. increase of pressure at constant temperature?
- What do you understand by the term partial molar free energy?
- State Gibbs–Duhem equation and its physical significance.
- State the relations that show variation of chemical potential of a component of system as a function of temperature and pressure.
- Van't Hoff reaction isotherm is useful for determining the feasibility of a reaction under a given set of conditions. Explain.
- Give names and mathematical expressions for equations representing variation of equilibrium constant with temperature and pressure.

Key Terms

Open, closed and isolated systems
Extensive and intensive properties
Isothermal, isochoric, isobaric processes
Reversible and irreversible processes
Internal energy
Heat
Work
First law of thermodynamics
Enthalpy
Heat capacity
Lavoisier and Laplace law
Hess's law
Kirchhoff's law
Joule–Thomson effect
Inversion temperature
Second law of thermodynamics
Entropy
Helmholtz's work function
Gibbs free energy
Gibbs–Helmholtz's equation
Spontaneity
Chemical potential
Gibbs–Duhem equation
Maxwell relations
Van't Hoff reaction isotherm
Law of mass action
Le Chatelier's principle

Objective-Type Questions

Multiple-Choice Questions

1. A process which involves change of state at constant volume is known as
   a. isobaric.
   b. isochoric.
   c. isothermal.
   d. adiabatic.
2. A system in thermodynamic equilibrium will be in
   a. thermal equilibrium.
   b. chemical equilibrium.
   c. mechanical equilibrium.
   d. All of the above.

3. Which one of the following is not an intensive property?
   a. Pressure
   b. Volume
   c. Temperature
   d. Time
4. Which of the following is an extensive property?
   a. Temperature
   b. Specific heat
   c. Heat capacity
   d. None of the above.
5. Which of the following is not a state property?
   a. Heat
   b. Internal energy
   c. Enthalpy
   d. Volume
6. Which of the following is not a correct expression for first law of thermodynamics?
   a. $\Delta E = q + W$
   b. $q = \Delta E + W$
   c. $q = \Delta E - W$
   d. $W = \Delta E - q$
7. The temperature of the system decreases in an
   a. adiabatic expansion.
   b. isothermal expansion.
   c. isothermal compression.
   d. adiabatic compression.
8. In an isothermal expansion of an ideal gas
   a. $\Delta E = 0$
   b. $W = 0$
   c. $\Delta V = 0$
   d. $q = 0$
9. Evaporation of water is
   a. an exothermic process.
   b. an endothermic process.
   c. a process where no heat change occurs.
   d. a process accompanied by chemical reaction.
10. For an exothermic process, enthalpy change ΔH is given by
    a. $\Delta H = 0$
    b. $\Delta H > 0$
    c. $\Delta H < 0$
    d. None of the above.
11. Bond energy of a substance
    a. is always positive.
    b. is always negative.
    c. is either positive or negative.
    d. depends upon the physical state of the system.
12. Joule–Thomson expansion for an ideal gas is an
    a. isochoric process.
    b. isobaric process.
    c. isothermal process.
    d. isoenthalpic process.
13. Which of the following is true for all natural processes which are spontaneous and irreversible?
    a. $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \geq 0$
    b. $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \leq 0$
    c. $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 0$
    d. None of the above.
14. Which of the following is not a spontaneous process?
    a. Diffusion of a gas from higher pressure to lower pressure
    b. Flow of heat from lower to higher temperature
    c. Precipitation of AgCl in the reaction $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$
    d. The reaction $H_2O(l, 25°C, 1\,atm) \rightarrow H_2O$ (vapor, 25°C, 1 atm)
15. Which of the following set of ΔH and ΔS values will lead to a spontaneous reaction?
    a. ΔH is positive and ΔS is negative.
    b. ΔH is positive and ΔS is positive (at low temperature).
    c. ΔH is negative and ΔS is positive.
    d. ΔH is negative and ΔS is negative (at high temperatures).
16. The variation of the heat of reaction with temperature is known as what?
    a. Van't Hoff isotherm

b. Van't Hoff isochore
c. Kirchhoff's equation
d. Clausius–Clapeyron equation

17. In a chemical reaction at equilibrium, ΔS = 25 J/K at 200 K, therefore ΔH is
a. 0 kJ
b. 5 kJ
c. 500 J
d. 50 kJ

18. A process is said to be at equilibrium when
a. $\Delta G = 0$
b. $\Delta G > 0$
c. $\Delta G < 0$
d. None of the above.

19. Which of the following is true for an equilibrium state?
a. Equal amounts of reactants and products are present.
b. The reactants are completely changed into products.
c. Small amount of product is formed and the reaction stops.
d. The rate of forward reaction is equal to rate of reverse reaction.

20. Which one of the following will decrease the equilibrium concentration of O_3 in the reaction?

$$NO_2(g) + O_2(g) \rightarrow NO(g) + O_3(g) - \text{heat}$$

a. Heating the mixture at constant pressure.
b. Increasing the pressure at constant temperature.
c. Adding more ozone.
d. Decreasing the pressure at constant temperature.

Fill in the Blanks

1. The path by which a system undergoes a change from an equilibrium state to another over a period of time is called a ________.
2. The quantity of heat required to raise the temperature of one mole of substance by 1°C is called ________.
3. The process in which heat is allowed to enter or leave the system but the temperature remains constant is called an ________ process.
4. In an ________ process, work is done by the system at the expense of its internal energy.
5. Heat is liberated in an ________ reaction.
6. For an ideal gas in isothermal process, change in internal energy is ________.
7. The entropy change for a spontaneous process is always ________.
8. Entropy of one mole of water is ________ than that of one mole of ice.
9. The chemical potential of a multicomponent system ________ with increase in temperature.

Review Questions

Short-Answer Questions

1. In terms of thermodynamics, what is a system? How are systems classified?
2. Define the thermodynamic terms: open system and closed system.
3. What is a state function? Give examples.
4. Distinguish between extensive and intensive properties.
5. Give differences between:

   a. Isothermal and adiabatic process
   b. Reversible and irreversible process
6. State the first law of thermodynamics and give its mathematical representation.
7. Define the terms internal energy and enthalpy and state the mathematical relation between them.
8. Why change of enthalpy does not depend on path?
9. Derive the expression for molar heat capacity using first law of thermodynamics.
10. What is the relation between C_p and C_V of an ideal gas?
11. For an isochoric process, show that change in internal energy is equal to heat exchanged between the system and surroundings.
12. In a reaction, change of enthalpy is more useful than change of internal energy. Explain.
13. For an isobaric process, show that enthalpy change of the system is equal to heat exchanged between system and surroundings.
14. State and illustrate Hess's law of constant heat summation.
15. a. State Lavoisier–Laplace law.
    b. For the reaction $C(s) + O_2(g) \rightarrow CO_2(g) +$ 393.5 kJ state the enthalpy change for combustion of carbon and decomposition of CO_2.
16. What is Kirchhoff's equation? State its significance.
17. What is Joule–Thomson effect? Define Joule–Thomson coefficient.
18. What is inversion temperature?
19. Is Joule–Thomson effect an adiabatic expansion?
20. What is entropy? What are the characteristics of entropy?
21. Predict the entropy changes in the following process:
    a. H_2O(at 25 °C and 1 atm) $\rightarrow$ H_2O(at 35 °C and 1 atm)
    b. $H_2O(l) \rightarrow H_2O$(vapor)
    c. H_2O (at 25 °C and 1 atm) $\rightarrow$ H_2O (at 25 °C and 10 atm)
22. State the second law of thermodynamics in terms of entropy and express it mathematically.
23. What is meant by a spontaneous process? Give examples of two chemical and two physical spontaneous changes?
24. What is free energy? What are its characteristics?
25. Show why free energy change should be negative for a spontaneous process, using the equation:

$$\Delta G = \Delta H - T\Delta S$$

26. Predict the nature of process for which (a) ΔH and ΔS are positive and (b) $\Delta H > 0$ and $\Delta S < 0$.
27. What is the significance of Gibbs–Helmholtz equation? How is it expressed mathematically?
28. What is work function? How is it related to entropy?
29. What happens to Helmholtz free energy at equilibrium ?
30. For a reaction, ΔH and ΔS both are positive. Under what condition will the reaction be spontaneous?
31. How is standard free energy change related to the equibrium constant?
32. For 1 mole of an ideal gas $T = f(p, V)$, show that dT is a perfect differential.
33. Consider the process : A(l, 1atm, 270 K) $\leftrightarrow$ A(S, 1 atm, 270 K). If the fusion temp. is 270 K, is this reaction spontaneous? Give reason.

34. State Gibbs–Duhem equation and its significance in a multicomponent open system.
35. Explain the term chemical potential or partial molar free energy of a multicomponent system.
36. Give the equation for Van't Hoff reaction isotherm and state its significance.
37. What are Maxwell relations? State Maxwell relations for internal energy, enthalpy, work function and Gibbs free energy.
38. State the law of mass action, and apply it to the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + Q$
39. a. What is Le-Chatelier's principle?
    b. What is the effect of pressure on the system $PCl_5 \rightleftharpoons PCl_3 + Cl_2$?
40. For the following reaction:

    $$2NO_2(g) \rightleftharpoons N_2O_4(g)\ (\Delta H = -58\ \text{kJ})$$

    Using Le Chatelier's principle for chemical equilibrium, explain the effect of following on position of equilibrium:
    a. increase in pressure at constant temperature
    b. increase in temperature at constant pressure
    c. addition of catalyst
41. Explain the effect of pressure and temperature on the following industrial reactions:

    $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22{,}000\ \text{cal}$$
    $$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) + 43{,}200\ \text{cal}$$

Long-Answer Questions

1. In terms of thermodynamics, what is a process? Describe the different types of processes by which a system changes from one state to another.
2. Discuss the application of first law of thermodynamics on an ideal gas, undergoing following processes:
   (a) isobaric,
   (b) isochoric,
   (c) isothermal and
   (d) adiabatic.
3. Derive the expressions for molar heat capacities Cp and C_V using first law of thermodynamics.
4. Discuss the limitations of first law of thermodynamics and the need for second law of thermodynamics.
5. What is enthalpy of a system? Show that at constant pressure, change in enthalpy is equal to heat absorbed by the system.
6. For a system undergoing irreversible change at constant temperature and pressure show that $\Delta G = W_{net}$ (where $W_{net} = W_{max} - W_{pressure\text{–}volume}$).
7. For an adiabatic process, prove that $pV^{\gamma} =$ constant.
8. Deduce the expression for the maximum work done when n moles of an ideal gas expand isothermally and reversibly.
9. Prove that adiabatic p–V curve would be steeper than the isotherm p–V curve.
10. Define Joule–Thomson coefficient and show that Joule–Thomson expansion is an isoenthalpic process.
11. State and explain the second law of thermodynamics. Explain the term entropy.
12. Evaluate the entropy changes in a reversible and irreversible process.
13. Derive the expression for entropy change on mixing of two ideal gases.
14. Write notes on (a) standard free energies and (b) Change in free energy of the system with variation in pressure for an isothermal process.

15. a. Show that $\left(\frac{\partial G}{\partial T}\right)_P = -S$
    b. For a reaction, ΔH and ΔS both are positive. Under what condition will the reaction be spontaneous?
    c. How is standard free energy change related to the equilibrium constant?
16. Derive the Gibbs–Helmholtz equation.
17. Explain the term chemical potential. Discuss its variation with temperature and pressure.
18. What are Maxwell relations? Derive any two of them.
19. Derive an expression for the variation of equilibrium constant of a reaction with temperature.
20. Derive the expression for pressure equilibrium constant and concentration equilibrium constant using the law of mass action.
21. Write notes on (a) Kirchhoff's law and derivation of its equation and (b) thermodynamic equilibrium.
22. Show that $\left[\frac{\partial}{\partial T}(\Delta G/T)\right]_p = -\frac{\Delta H}{T^2}$
23. Show that $\left[\frac{\partial (G/T)}{\partial (1/T)}\right]_p = H$
24. Show that $\left(\frac{\partial G}{\partial p}\right)_T = V$
25. Show that $C_p - C_V = \left[V - \left(\frac{\partial H}{\partial p}\right)_T\right]\left(\frac{\partial p}{\partial T}\right)_V$

Numerical Problems

1. Calculate the work done and heat absorbed when 60 g of argon expands isothermally at 57°C from 5 atm to 0.5 atm.
2. A gas expands against a variable external pressure given by $p = 10/V$ atm, where V is the volume at each stage of expansion. In expanding from 10 l to 100 l, the gas undergoes a change in internal energy $\Delta E = 100$ cal. How much heat has been absorbed?
3. If 22 grams of CO_2, showing ideal behavior, expand isothermally and reversibly from 2.5 l to 7.5 l at 27°C. Calculate the work done and heat absorbed.
4. Calculate the change in internal energy for the combustion of ethane, if heat of reaction at 25°C and constant pressure is $\Delta H^o = -1560$ kJ/mol.
5. Calculate the final volume of 10 g CO_2 (behaving ideally) initially at 0°C and 1 atm pressure if it undergoes reversible isothermal expansion after absorbing 25 kJ of heat.
6. Assuming that water vapor shows ideal gas behavior, calculate ΔH and ΔE when 72 g water undergoes reversible isothermal evaporation at 100°C, given that heat of evaporation of water is 540 cal/g.
7. Calculate the enthalpy change for the following reaction:

   $$2H_2S(g) + 3O_2(g) \rightarrow 2\ H_2O(l) + 2SO_2(g)$$

   Given that standard heats of formation of H_2S, H_2O and SO_2 are: –20.1 kJ/mol, –285.8 kJ/mol and –296.9 kJ/mol, respectively.
8. Calculate the enthalpy of combustion of glucose from the following data:
    a. $C(s) + O_2(g) \rightarrow CO_2(g)$

       $\Delta H^o = -393.5$ kJ
    b. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

       $\Delta H^o = -286$ kJ

c. $6C(s) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s) \quad \Delta H^o = -1260$ kJ

9. Compute the enthalpy of formation of nitric oxide using the following data:

$$NO(g) + CO(g) \rightarrow \tfrac{1}{2}N_2(g) + CO_2(g)$$

$$\Delta H^o = -372.2 \text{ kJ/mol}$$

where $\Delta H_f^o(CO) = -110.5$ kJ/mol and

$$\Delta H_f^o(CO_2) = -393.5 \text{ kJ/mol}$$

10. Calculate the entropy change when 1.8 g of water is completely converted into vapor at 100°C. The molar heat of vaporization is 40.85 kJ/mol.

11. What is the boiling point of a liquid with entropy of vaporization 68.3 J/K/mol and enthalpy of vaporization 35.65 kJ/mol?

12. Calculate the change in entropy when 84 g of CO, behaving as an ideal gas, expands isothermally to three times its initial volume. What would be the change in entropy when the gas is heated from 25°C to 55°C at constant volume, given that $C_p = 2.5\,R$.

13. Calculate the increase in entropy when 3.4 l of oxygen is mixed with 12.4 l of hydrogen at standard conditions of temperature and pressure.

14. Calculate the equilibrium constant for a reaction at 400 K given that $\Delta H^o = 268.3$ kJ/mol and $\Delta S = 0.857$ kJ/K/mol at 400 K.

15. The equilibrium constant for the reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} atm at 400°C and 0.144×10^{-4} atm at 500°C. Calculate the heat of formation of one mole of ammonia from its elements in the given temperature range.

16. For CO_2 (g) at 300 K and 1 atm pressure $(\partial H/\partial p)_T = -10.2$ cal/mol/atm and $C_p = 8.919$ cal/mol/K. Calculate the Joule–Thomson coefficient of the gas for the given temperature and pressure conditions.

Answers

Multiple-Choice Questions

1. (b)
2. (d)
3. (d)
4. (c)
5. (a)
6. (b)
7. (a)
8. (a)
9. (b)
10. (c)
11. (a)
12. (d)
13. (a)
14. (b)
15. (c)
16. (c)
17. (b)
18. (a)
19. (d)
20. (c)

Fill in the Blanks

1. process
2. molar heat capacity
3. isothermal
4. adiabatic

5. endothermic
6. zero
7. positive
8. more
9. decreases

Numerical Problems

1. $W = 332.98$ cal; $q = 332.98$ cal
2. $q = 661.5$ cal
3. $W = 327.4$ cal; $q = 327.4$ cal
4. $\Delta E = -1553.8$ kJ/mol
5. $V_2 = 285.8$ l
6. $\Delta H = 38880$ cal; $\Delta E = 35915.4$ cal
7. $\Delta H = 1125.5$ kJ/mol
8. $\Delta H = -2817$ kJ/mol
9. $\Delta H^{o}_{f(NO)} = 89.2$ kJ/mol
10. $\Delta S = 10.95$ J/K
11. $T = 248.96$°C
12. $\Delta S = 6.55$ cal/K; $\Delta S = 0.852$ cal/K
13. $\Delta S_{mixing} = 3.04$ J/K
14. $K = 9.376 \times 10^{3}$
15. $\Delta H^{o}_{f(NH_3)} = 52.63$ kJ/mol
16. $\mu = 11.44$ K/atm

6

Phase Equilibria

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Concept of phase, component and degree of freedom.
- Determination of number of phases, components and degrees of freedom in a system.
- Derivation of phase rule.
- Advantages and limitations of phase rule.
- Clausius–Clapeyron equation.
- Interpretation of phase diagrams for one-component system (water and sulphur systems).
- Interpretation of phase diagrams for two-component system (Cd–Bi and Fe–C systems).

Phase rule was derived by J. Willard Gibbs in 1876 and it is considered as one of the greatest generalizations in Physical Chemistry. The phase rule was further developed by H.W.D. Roozeboom, Ostwald, Van′t Hoff and others. A system containing more than one phase is called a heterogeneous system. Phase rule summarizes important limitations on heterogeneous systems at equilibrium.

6.1 Definition of Terms

Phase

A phase can be defined as the form of matter which is uniform throughout in chemical composition and physical state. In a heterogeneous system, a phase is separated from the other parts of the system by distinct physical boundaries. Typical phases are solid, liquid and gaseous. For example, ice (solid phase), water (liquid phase) and water vapor (gaseous phase) are three phases of the same chemical substance water.

In systems consisting entirely of gases, only one phase can exist in equilibrium because all gases are miscible in all proportions. Liquids that are completely miscible with each other constitute one phase only. For example, ethyl alcohol mixed with water constitutes a single phase. The immiscible liquids separated by distinct boundary are two different phases. Many different phases can coexist for one solid substance (e.g., rhombic and monoclinic sulphur). Mere difference in shape or in degree of subdivision is not enough to determine a new phase. Thus, many pieces of ice floating on water constitute only one solid phase, that is, ice. Similarly, many droplets of water on a surface represents only one phase. In a heterogeneous mixture of solids, the number of phases is equal to the number of solid substances present in the mixture. Phases that have properties between liquids and solids are called **mesomorphic**.

The number of phases present in different physical states are given as follows:

1. A gaseous mixture is a single phase, irrespective of the number of constituent gases present, as a gaseous mixture is always homogeneous. Thus, a mixture of N_2, O_2 and CO_2 constitute a single phase.
2. A mixture of two or more liquids that are completely miscible with each other also constitutes a single phase. For example, a mixture of ethanol, methanol and water constitutes only one phase.
3. A mixture of two or more immiscible liquids does not constitute a single phase as definite boundaries exist in the system separating the layers from each other. Thus, a mixture of water and oil constitutes two phases.
4. The number of phases present in a heterogeneous mixture of solids is equal to the number of solid substances present in the mixture. Hence a mixture of $CaCO_3$ and CaO constitute two phases.
5. A solid solution is considered as a single phase because it is a homogeneous mixture. For example, solid solution of copper and gold is a single phase.
6. The solution of a substance in a solvent consists of one phase. For example, solution of sugar in water is a single phase.

Component

The components can be defined as the minimum number of chemically independent species which are required to express the composition of all the phases present in the system. Thus, the number of components is not the same as the total number of chemical constituents or chemical species present in the system. The actual choice of the components (out of the total chemical species present) in a system is purely a matter of convenience. The number of independent components may be easily calculated from the number of different chemical species present minus the number of chemical equations connecting them. Mathematically, we can write it as:

$$C = N - E$$

where C is the number of components, N is the total number of chemical species present and E is the number of independent equations relating the chemical species.

The following examples show the number of components in different systems:

1. Water system consisting of ice, water and vapor is a three-phase system, but the number of components in the system is only one because all the phases can be represented by the chemical formula of water, that is, H_2O.
2. The decomposition of $CaCO_3$ in vacuum is given according to the equation:

$$\mathrm{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$$

   The system consists of three phases (two solid and one gas) and the number of constituents is three ($CaCO_3$, CaO and CO_2). But these three constituents are not chemically independent. The composition of all the three phases can be expressed with the help of any two constituents (out of three). Hence, it is considered as a two-component system. For example,
   - When CaO and CO_2 are taken as components

$$\mathrm{CaCO_3 = CaO + CO_2}$$
$$\mathrm{CaO = CaO + 0CO_2}$$
$$\mathrm{CO_2 = 0CaO + CO_2}$$

- When $CaCO_3$ and CO_2 are taken as components

$$\begin{aligned} CaCO_3 &= CaCO_3 + 0CO_2 \\ CaO &= CaCO_3 - CO_2 \\ CO_2 &= 0CaCO_3 + CO_2 \end{aligned}$$

- When $CaCO_3$ and CaO are taken as components

$$\begin{aligned} CaCO_3 &= CaCO_3 + 0CO_2 \\ CaO &= 0CaCO_3 + CaO \\ CO_2 &= CaCO_3 - CaO \end{aligned}$$

3. The decomposition of NH_4Cl in vacuum is given according to the following equation:

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

The system consists of two phases, solid NH_4Cl and a gaseous mixture of NH_3 and HCl. Since the proportion of NH_3 and HCl is the same in gaseous mixture as it is in the solid NH_4Cl, the two phases can be expressed by the same chemical formula, that is, NH_4Cl. Hence, this system is a one-component system.

If an excess of NH_3 or HCl is added to the system, the number of components increases to two because the vapor phase no longer has the same composition as the solid NH_4Cl.

4. PCl_5 dissociates on heating in vacuum according to the following equation:

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g) \tag{6.1}$$

Three phases are present in the system, namely, solid (PCl_5), liquid (PCl_3), gas (Cl_2). The number of chemical species present is three but they are not chemically independent but related through the chemical equation, Eq. (6.1).
Hence the number of components is $C = N - E = 3 - 1 = 2$.
Therefore, it is a two-component system.

5. $CaSO_4$ dissociates on heating in vacuum according to the following equation:

$$2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g) \tag{6.2}$$

The number of phases present is three (two solid and one gas). The number of chemical species present is four ($CaSO_4$, CaO, SO_2 and O_2). There is one chemical equation, Eq. (6.2) relating the constituents. Additionally, in the gaseous phase, the molar ratio of SO_2 and O_2 is fixed (SO_2:O_2 = 2:1). Hence the number of components $C = N - E = 4 - 2 = 2$.

6. System formed by water and two salts without a common ion, for example, KNO_3 and NaI in water. In this system, four different salts or their hydrates may occur in solid phases, namely, KNO_3, NaI, KI and $NaNO_3$. To specify the composition of all possible phases, four components are necessary consisting of water and any three of the possible four salts. Hence, it is a four-component system.

Degree of Freedom or Variance

The degree of freedom of a system can be defined as the smallest number of intensive variables (such as temperature, pressure and concentration) that can be changed independently without disturbing the number of phases in equilibrium. For example,

1. The state of a certain amount of pure gas may be described completely by any two of the three variables: pressure, temperature and density. If any two are known, the third can be calculated. This system, therefore, has two degrees of freedom or it is a bivariant system.
2. In the system where water and water vapor are in equilibrium, only one intensive variable is required to describe the state. At any given temperature, the pressure of vapor in equilibrium with liquid water is fixed in value. The system, therefore, has one degree of freedom or it is a univariant system.
3. If all the three phases of water, that is, ice, water and vapor exist in equilibrium, no condition needs to be specified as the three phases can coexist only at a particular value of temperature and pressure. The system, therefore, has no (zero) degree of freedom and it is called invariant or non-variant system. If the temperature or pressure is changed, the three phases will not remain in equilibrium and one of the phases will disappear.

6.2 Phase Rule

Gibbs phase rule states that for every heterogeneous system in equilibrium, the sum of the number of phases and degrees of freedom is greater than the number of components by 2. Mathematically, we can represent it as:

$$P + F = C + 2$$

or

$$F = C - P + 2$$

where P is the number of phases in equilibrium, C is the number of components and F is the number of degrees of freedom.

Derivation of Phase Rule

Consider a system in equilibrium consisting of C components distributed between P phases. Each component will be distributed between P phases.

1. For thermal equilibrium between P phases, the temperature must be the same for every phase, that is, there will be only one value of temperature.
2. For mechanical equilibrium between P phases, the pressure must be same for every phase, that is, there will be only one value of pressure.
3. For material equilibrium between P phases, the chemical potential value μ of each component must have the same value in every phase.

Let μ_{ij} being the chemical potential of ith component in jth phase. For the first component, chemical potential must be same in every phase:

$$\mu_{11} = \mu_{12} = \mu_{13} = \cdots = \mu_{1P} \quad \text{(total } P-1 \text{ equations)}$$

Similarly, for the second component chemical potential must be same in every phase:

$$\mu_{21} = \mu_{22} = \mu_{23} = \cdots = \mu_{2P} \quad \text{(total } P-1 \text{ equations)}$$

Similarly for the Cth component chemical potential must be same in every phase:

$$\mu_{C1} = \mu_{C2} = \mu_{C3} = \cdots = \mu_{CP} \quad \text{(total } P-1 \text{ equations)}$$

Therefore, for C components the total number of equations relating chemical potentials = $C(P-1)$.

We know that in a given phase involving C components at temperature T and pressure P, the chemical potential is determined by the mole fractions of the components present. However, for each phase, the sum of mole fractions of all components is unity, implying that at most $(C - 1)$ mole fractions can be independent. Therefore, for P phases, there are at most $P(C - 1)$ independently variable mole fractions. In addition, the temperature and pressure are two other intensive variables of the system. Hence, the total number of independently variable properties of the system = $P(C - 1) + 2$. However, these $P(C - 1) + 2$ variables are related to each other through $C(P - 1)$ equations (between chemical potentials). Hence,

$$\begin{bmatrix}\text{Total number of independent}\\ \text{intensive variables}\end{bmatrix} = \begin{bmatrix}\text{Total number of variables}\end{bmatrix} - \begin{bmatrix}\text{Total number of equations}\\ \text{connecting the variables}\end{bmatrix}$$

$$\begin{aligned} F &= P(C-1)+2-C(P-1)\\ &= PC-P+2-PC+C\\ &= C-P+2 \end{aligned}$$

This is Gibbs phase rule.

Advantages of Phase Rule

1. It provides a convenient method for classification of equilibrium states of system with the help of phases, components and degrees of freedom.
2. It predicts the behavior of system with changes in the intensive variables, such as temperature, pressure and composition.
3. It indicates that different systems having the same number of degrees of freedom behave in the same manner.
4. It is applicable to macroscopic system and therefore information about the molecular structure is not necessary.
5. It takes no account of nature of the reactants or products in phase.
6. It is applicable to physical as well as chemical equilibria.

Limitations of Phase Rule

1. It is applicable only for the systems in equilibrium, therefore it is of no use for the systems which attain the state of equilibrium very slowly.
2. It is applicable to a single equilibrium state and does not indicate about the other possible equilibrium states in the system.
3. It considers only the intensive variables such as temperature, pressure and concentration (or composition). It does not consider the other factors such as influence of electric or magnetic field.
4. It considers only the number of phases, but does not take into consideration the quantity of phases.
5. It requires that the solid and liquid phases are not present in such finely divided form that deviation in vapor pressure (from the normal values) takes place.
6. It requires all the phases to be present under the same conditions of temperature and pressure.

Concept Check

- State the Gibbs phase rule. How is it expressed mathematically?
- State three limitations of the phase rule.
- List two important advantages of the phase rule.

6.3 Clausius–Clapeyron Equation

We have seen that for a given pressure, phase transition between two states of a system takes place at a fixed temperature. However, this temperature varies with change in pressure. The temperature for phase transitions at different pressures can be related using the laws of thermodynamics. Consider a system consisting of one mole of a substance, which exists in two phases A and B at temperature T and pressure p. Let the free energy of the substance (per mole) in the two phases be G_A and G_B. Since the system is in equilibrium, so there is no free energy change, that is

$$G_A = G_B$$

Let the temperature of the system be raised to $T + dT$, so that pressure becomes $p + dp$. The free energies of the system in two phases will then be given by $G_A + dG_A$ and $G_B + dG_B$, respectively. As the two phases are still in equilibrium, so

$$G_A + dG_A = G_B + dG_B$$

The variation in free energy with change in temperature and pressure is given by the relation:

$$dG = Vdp - SdT \tag{6.3}$$

When the phases are in equilibrium, work done is due to volume change only, so Eq. (6.3) may be applied to both the phases as:

$$dG_A = V_A dp - S_A dT \tag{6.4}$$

$$dG_B = V_B dp - S_B dT \tag{6.5}$$

where V_A and V_B are the volumes (per mole) of phases A and B, respectively, and S_A and S_B are their molar entropies. At equilibrium, $dG_A = dG_B$, so from Eqs. (6.4) and (6.5) we get

$$V_A dp - S_A dT = V_B dp - S_B dT$$

or

$$\frac{dp}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\Delta S}{V_B - V_A} \tag{6.6}$$

where ΔS is the molar entropy change and $V_B - V_A$ is the change in volume when one mole of substance changes from phase A to B. This is known **Clapeyron equation** and it relates the change in temperature that accompanies change in pressure in a system with two phases in equilibrium. Since phase change is a reversible isothermal process,

$$\Delta S = \frac{q}{T} = \frac{\Delta H}{T} \tag{6.7}$$

where q is the heat absorbed or ΔH is the enthalpy change per mole of substance at temperature T. Equation (6.6) may be written as:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T(V_B - V_A)} \tag{6.8}$$

For a liquid–vapor equilibrium (vaporization),

$$\Delta V = V_g - V_l \approx V_g \quad (\text{as } V_g >> V_l)$$

Similarly for a solid–vapor equilibrium (sublimation),

$$\Delta V = V_g - V_s \approx V_g \quad (V_g >> V_s)$$

Assuming that the vapor shows ideal gas behavior, we have

$$V_g = \frac{RT}{p}$$

Substituting in Eq. (6.8) we get

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H p}{RT^2} \quad \text{or} \quad \frac{1}{p}\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \quad \text{or} \quad \frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \quad \text{or} \quad \mathrm{d}\ln p = \frac{\Delta H}{R} \times \frac{\mathrm{d}T}{T^2}$$

This is known as the **Clausius–Clapeyron** equation. Integrating the equation over small range of temperature (T_1, T_2) and pressure (p_1, p_2) over which ΔH remains constant, we get

$$\ln\frac{p_2}{p_1} = \frac{\Delta H}{R} \times \frac{T_2 - T_1}{T_1 T_2} \tag{6.9}$$

The *Clausius–Clapeyron* equation can be used to calculate:

1. The change in boiling point of liquid with change in pressure.
2. Latent heat of vaporization if boiling points of a liquid at two different vapor pressures is known.
3. Latent heat of fusion if melting points of a solid at two different vapor pressures is known.

6.4 One-Component Systems

The phase diagram of a one-component system is a two-dimensional representation of the dependence of the equilibrium state of existence of the system on the two independent intensive variables. Pressure and temperature are chosen as two independent variables representing the two axes in the phase diagram.

Water System

This system consists of only one component, namely, water represented by the chemical formula H_2O. Water exists in three possible phases: ice (solid), water (liquid) and water vapor (gas). It is a one-component system, therefore, the maximum number of degrees of freedom in this system is two when only one phase is stable at equilibrium ($F = C - P + 2 = 1 - 1 + 2 = 2$). The phase diagram for water is a two-dimensional plot where pressure and temperature are taken as axes and is represented in Figure 1.

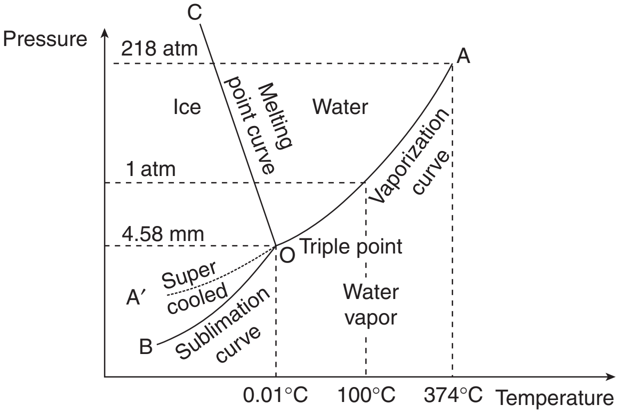


Figure 1 Phase diagram of water.

The Areas (Bivariant Systems)

The phase diagram of water is divided into three areas by the lines BO, OC and OA. Area BOC represents the conditions of temperature and pressure, where only ice is capable of stable existence. Similarly, areas COA and BOA represent the conditions for the stable existence of water and water vapor, respectively. In order to define the system completely, it is necessary to specify both the temperature and pressure. Therefore, the areas representing ice, water and water vapor have two degrees of freedom and are called bivariant systems. The phase rule also predicts the same degrees of freedom:

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

The Curves (Univariant Systems)

1. **Curve OC (Melting point curve** or **freezing point curve):** Curve OC represents the equilibrium between ice and water. It is also called **fusion curve** of ice as it indicates the temperature and pressure at which ice (solid) and water (liquid) can coexist at equilibrium. In other words, this curve shows the effect of pressure on the melting point of ice. As shown in the Figure 1, line OC is inclined towards the pressure axis (i.e., negative slope of the curve), which indicates that melting point of ice is increased by lowering pressure. It can also be predicted from Clausius–Clapeyron equation as follows

$$\frac{dp}{dT} = \frac{\Delta H_{\text{fusion}}}{T(V_l - V_s)} \tag{6.10}$$

where V_l is the volume of water, V_s is the volume of ice and ΔH_{fusion} is the enthalpy of fusion. Equation (6.10) can be written as

$$\frac{dT}{dp} = \frac{T(V_l - V_s)}{\Delta H_{\text{fusion}}} \tag{6.11}$$

We know that density of ice is less than that of water. So, volume of ice (V_s) is larger than that of water (V_l), due to which the expression on right hand side of Eq. (6.11), becomes negative. This means, dT/dp will be negative. The negative value of dT/dp indicates that increase of pressure must lower the freezing point of water or the melting point of ice is increased by decreasing pressure. This is evident from the Figure 1 that the melting point of ice is 0° C at 1 atm (760 mm) pressure, which is increased to 0.01°C, when the pressure is decreased to 4.58 mm.

In order to describe the system completely, it is enough to know either temperature or pressure, because the other variable gets automatically fixed. For example at atmospheric pressure, ice and water can be in equilibrium only at one temperature, that is, at the freezing point of water. Thus ice–water equilibrium line (curve OC) has only one degree of freedom or it is a univariant system. We get the same result by applying phase rule equation:

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

2. **Curve OA (Vaporization curve** or **vapor pressure curve):** The curve represents the equilibrium between water and vapor. It shows the vapor pressure of liquid water at different temperatures and is called **vapor pressure curve** of water. In order to describe the system along the line OA, it is enough to know either temperature or pressure as the other variable gets automatically fixed. This is because at any temperature, the pressure of vapor in equilibrium is fixed in value. Thus water–vapor equilibrium line (curve OA) has only one degree of freedom or it is a univariant system. We get the same result by applying phase rule equation:

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

At the higher end, the curve OA terminates at the point A which corresponds to the critical temperature (374°C) and pressure (218 atm) of water since liquid water cannot exist above this temperature.

The variation of vapor pressure with temperature can be given by Clausius–Clapeyron equation as

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T(V_g - V_l)} \tag{6.12}$$

where V_g is the volume of water vapor, V_l is the volume of water and ΔH_{vap} is the enthalpy of vaporization.

We know that $pV = RT$, which implies that

or $$V = \frac{RT}{p}$$

Since, $V_g >> V_l$, $V_g - V_l = V_g = RT/p$. Substituting the value of V_g in Eq. (6.12), we get,

$$\frac{dp}{dT} = \frac{p\Delta H_{vap}}{RT^2}$$

or $$\frac{dp}{p} = \frac{\Delta H_{vap}}{R}\frac{dT}{T^2} \tag{6.13}$$

Integrating Eq. (6.13), we get

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] \tag{6.14}$$

3. **Curve OB (Sublimation curve):** Curve OB represents the conditions for the equilibrium between ice and vapor. It shows the vapor pressure of ice at different temperatures and is called **sublimation curve** of ice. In order to describe the system along the line OB, either the value of temperature or pressure need to be specified. Because at any temperature, the value of vapor pressure of ice is fixed. Thus, ice–vapor equilibrium curve (curve OB) has only one degree of freedom or it is a univariant system. This follows from phase rule equation also:

   $$F = C - P + 2 = 1 - 2 + 2 = 1$$

   At the lower limit, the curve OB terminates at absolute zero temperature where vapor pressure is zero and only ice can exist. The variation of vapor pressure of ice with temperature is given by Clausius–Clapeyron equation as

   $$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\text{sub}}}{T(V_{\mathrm{g}} - V_{\mathrm{s}})} \tag{6.15}$$

   where V_{g} is the volume of water vapor, V_{s} is the volume of ice and ΔH_{sub} is the enthalpy of sublimation.
   Since $V_{\mathrm{g}} >> V_{\mathrm{s}}$, $V_{\mathrm{g}} - V_{\mathrm{s}} = V_{\mathrm{g}} = RT/p$. Substituting the value of $V_{\mathrm{g}} - V_{\mathrm{s}}$ in Eq. (6.15), we get

   $$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_{\text{sub}}\, p}{RT^2}$$

   or

   $$\frac{\mathrm{d}p}{p} = \frac{\Delta H_{\text{sub}}}{R}\frac{\mathrm{d}T}{T^2} \tag{6.16}$$

   Integrating Eq. (6.16), we get

   $$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{sub}}}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] \tag{6.17}$$

4. **Curve OA′:** Sometimes, it is possible to cool water below its freezing point without formation of ice. The water is then said to be supercooled and can be kept as such until a small piece of ice comes in contact with it. Therefore, the vapor pressure curve of liquid water AO can continue below the point O. It is shown by dotted line OA′ in the Figure 1.This liquid–vapor system along OA′ is said to be in metastable equilibrium since water can be converted to ice, when a small piece of ice comes in contact with the supercooled liquid. Hence, curve OA′ is called the vapor pressure curve of metastable water. It is seen from the phase diagram that curve OA′ lies curve above curve OB. Thus, the metastable system has a higher vapor pressure than the stable one at the same temperature.

Triple Point O

The point O where the three curves OC, OA and OB meet is known as **triple point**. This is the point where the three phases of water, that is, ice, water and vapor coexist in equilibrium. The triple point corresponds to a temperature of 0.01°C and a pressure of 4.58 mm Hg. The degree of freedom at this point is zero as there are three phases in equilibrium for a one-component system. This follows from the phase rule also.

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Hence, the system is non-variant at triple point and it is not possible to change the value of either temperature or pressure. Upon changing either temperature or pressure, the three phases would no longer coexist and at least one of them would disappear.

Sulphur System

The sulphur system is an one-component system. Sulphur is the component which is represented by the symbol S. It exists in four phases: rhombic sulphur (S_R), monoclinic sulphur (S_M), liquid sulphur (S_L) and sulphur vapor (S_V). Sulphur system is a classical example of a system which exhibits solid–solid transformation between two different crystalline forms of the same substance.
According to the phase rule for a one-component system,

$$F = C - P + 2 = 1 - P + 2 = 3 - P$$

or

$$P = 3 - F$$

As the minimum value of F is zero, the maximum number of phases that can exist simultaneously is three. Therefore, all the four phases of sulphur cannot exist simultaneously, but any of the three phases can coexist. The phase diagram of the sulphur system is represented in Figure 2.

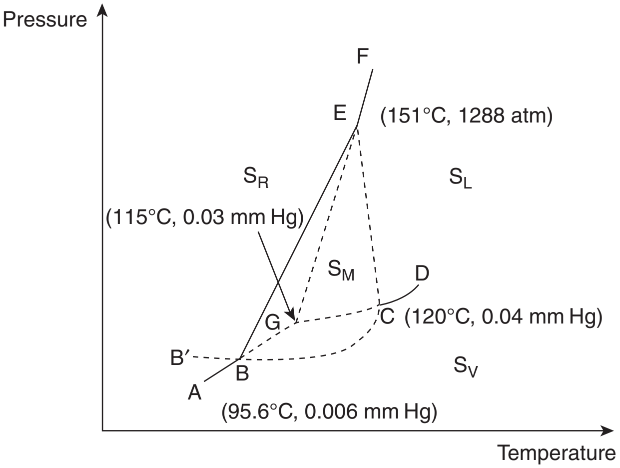


Figure 2 Phase diagram for sulphur system.

Areas (Bivariant System)

1. **Area below ABCD:** Only sulphur vapor (S_V) exists in this region.
2. **Area right to DCEF:** Only liquid sulphur (S_L) exists in this region.
3. **Area left to ABEF:** Only rhombic sulphur (S_R) exists in this region.

4. **Area BCE:** Only monoclinic sulphur (S_M) exists in this region.

In all the above areas, only one phase exists and in order to define the system completely, two variables, that is, pressure and temperature are needed. Hence, the areas represent a bivariant system. We get the same result from phase rule: $F = C - P + 2 = 1 - 1 + 2 = 2$.

Curves (Univariant Systems)

1. **Curve AB (Sublimation curve):** It is the sublimation or vapor pressure curve of S_R. This curve represents the equilibrium between S_R and S_V. The system has one degree of freedom. Point B is the transition point for the transition between two crystalline states of sulphur $S_R \rightleftharpoons S_M$. This transition takes place at 95.6°C. At the transition temperature, both S_R and S_M are stable, but below this temperature only S_R is stable and S_M slowly changes into S_R. If S_R is heated extremely slowly, it gradually changes to S_M.
2. **Curve BC:** It is the sublimation or vapor pressure curve of S_M. This curve represents the equilibrium between S_M and S_V. The system has one degree of freedom. The dotted curve BB′ is the extension of the curve BC and represents the vapor pressure curve of metastable S_M.
3. **Curve CD:** It is the vapor pressure curve of S_L. This curve represents the equilibrium between S_L and S_V. At higher end, the curve CD terminates at D which is the critical temperature of sulphur where only one fluid phase exists.
4. **Curve BE:** It is the transition curve and represents the equilibrium between S_R and S_M. This curve shows the effect of pressure on transition temperature of S_R in to S_M. Both the phases are solid and the system is monovariant. As shown in the Figure 2, curve BE slopes away from the pressure axis. This means, the slope of this curve is positive, which indicates that the transition temperature between S_R and S_M is raised by the increase of pressure. This can also be predicted with the help of Clausius–Clapeyron equation.

$$\frac{dp}{dT} = \frac{\Delta H_t}{T(V_M - V_R)} \tag{6.18}$$

   where V_M is the volume of monoclinic sulphur, V_R is the volume of rhombic sulphur and ΔH_t is the enthalpy of phase transition from S_R to S_M.

   Since density of S_M is less than that of S_R, volume of S_M is larger than that of S_R. Right hand side of Eq. 6.18 is therefore positive, which results in the positive value of dp/dT. It means that increase in pressure raises the transition temperature of S_R in to S_M. The curve BE terminates at point E beyond which S_M disappears.
5. **Curve CE:** It is the melting point or fusion curve of S_M. This curve represents the equilibrium between S_M and S_L. Hence its degree of freedom is one or it is monovariant. Curve CE represents the effect of pressure on melting point of S_M. As shown in the Figure 2, curve CE slopes away from the pressure axis. This means, the slope of this curve is positive, which indicates that the melting point of S_M is raised by the increase of pressure. This can also be predicted with the help of Clausius–Clapeyron equation.

$$\frac{dp}{dT} = \frac{\Delta H_f}{T(V_L - V_M)} \tag{6.19}$$

   where V_M is the volume of monoclinic sulphur, V_L is the volume of liquid sulphur and ΔH_f is the enthalpy of fusion of S_M.

As the melting of S_M is accompanied by slight increase of volume, $V_L > V_M$, that is, volume of liquid sulphur is greater than that of monoclinic sulphur. This indicates that the term at the right hand side of Eq. (6.19) is positive. So dp/dT is positive, which shows that the melting point of S_M is raised by the increase of pressure.

6. **Curve EF:** It is the melting point curve or fusion curve of S_R. There exist equilibrium between S_R and S_L. So the system is monovariant.
7. **Curve BG:** This curve is the extension of curve AB. It represents the metastable equilibrium between S_R and S_V. If temperature of S_R is allowed to rise quickly at about 95.6°C, it changes to sulphur vapor (S_V) without changing into monoclinic sulphur (S_M). Hence a metastable equilibrium exists between S_R and S_V. This occurs because the conversion of one solid form (S_R) to another solid form (S_M) involves molecular rearrangement, which is a slow process. Unless heating is carried out extremely slowly, there is a possibility that S_R may not change into S_M at the transition temperature (95.6°C). As a result S_R will exist in metastable equilibrium with its vapor.
8. **Curve CG:** If liquid sulphur (S_L) is allowed to cool along the curve DC, the solid phase may not separate out at C unless cooling is carried out extremely slowly. The line CG represents the metastable equilibrium between liquid sulphur and its vapor.
9. **Curve EG:** It gives the effect of pressure on the melting point of S_R. In other words this is the fusion curve of metastable S_R.

Triple Points

1. Triple point B represents the equilibrium between S_R, S_M and S_V. It corresponds to the temperature of 95.6°C and pressure of 0.006 mm Hg.
2. Triple point C represents the equilibrium between S_M, S_L and S_V. It corresponds to the temperature of 120°C and pressure of 0.04 mm Hg.
3. Triple point E represents the equilibrium between S_M, S_L and S_R. It corresponds to the temperature of 151°C and pressure of 1288 atm.
4. Metastable triple point G represents the equilibrium between S_R, S_L and S_V. It corresponds to the temperature of 115°C and pressure of 0.03 mm Hg.

Concept Check

- What is the maximum number of degrees of freedom possible for water system?
- What is the significance of Clapeyron equation?
- Clausius–Clapeyron equation may be used to calculate latent heat of transformation from one phase to another. Explain.
- In the phase diagram of water system, what is the significance of triple point?
- In the phase diagram of water, what is the degree of freedom in areas representing the solid, liquid or gaseous state and along the boundary lines between the phases?
- Explain how it is possible to cool water below its freezing point without solidification.
- How many triple points are possible for the sulphur system? What are the phases in equilibrium at these points?
- In the phase diagram of the sulphur system, explain the significance of the following observations:
  - **a.** Curve representing equilibrium between monoclinic and rhombic forms slopes away from the pressure axis.
  - **b.** Curve between sulphur monoclinic and liquid sulphur slopes to the right.

6.5 Two-Component Systems

In two-component systems with $P = 1$, the number of degrees of freedom are of highest order, three. In these cases, the phase diagram may be represented by a three-dimensional diagram of pressure, composition and temperature. In practice, however, the phase diagrams for a two-component system are represented by plane diagrams with two axes representing two variables, while the third variable is held constant. The phase diagrams may be constructed as

1. Pressure–temperature diagram (p–T) keeping concentration constant.
2. Pressure–concentration diagram (p–C) keeping the temperature constant.
3. Temperature–concentration diagram (T–C) keeping the pressure constant.

Solid–Liquid Equilibria

In the phase rule equation, when pressure is kept constant, the vapor phase of the system is not considered. In that case, the system is said to be condensed and phase rule for such a system reduces to:

$$F' = C - P + 1$$

This is called **condensed** or **reduced** phase rule. Temperature vs. composition diagrams are drawn to represent the solid–liquid equilibria. For this purpose, the composition of the mixture at different temperatures is determined at atmospheric pressure.

The two-component solid–liquid equilibrium may be classified depending on the miscibility of the two components in molten state and also on the nature of solid phases that separate out on cooling. The two components may either be completely or partially miscible in the liquid state. When the two components that are completely miscible in liquid state are allowed to cool to a low temperature, components begin to separate out as solids in any of the following three forms:

1. The components are not miscible in solid state and form eutectic mixtures, for example, lead–silver alloy.
2. The components form a stable solid compound, which melts at a constant temperature to give a liquid with the same composition as the solid compound. Such compounds are said to have congruent melting points.
3. The components form a solid compound, which is unstable and decomposes below its melting point to give a new solid phase, and a liquid that is different in composition from the original compound. Such compounds are said to have incongruent melting points.

Construction of the Phase Diagram

Detecting a phase change in two-component system is not always as simple as detecting the melting point of ice or boiling point of water. Thermal analysis is the most widely used technique for detecting the phase transitions in such systems. In this method, a mixture of known composition, say of two components A and B, is heated to a high enough temperature so that it is homogeneous. Then it is allowed to cool at a regulated rate and its temperature is monitored with respect to time. At a certain temperature called the freezing temperature, a solid will start appearing. The curves obtained are termed as cooling curves and are used to construct the phase diagram of a system.

At a phase transition, usually from liquid to solid, heat is evolved and the cooling stops until the transition is complete. This shows as an infliction in the cooling curve, which is used mark a transition point in the phase diagram.

This process is repeated for various compositions, and thereby we get various transition points. By joining these points we can construct the phase diagram for the system. The solid–liquid boundary is represented by the points at which the rate of cooling changes. A plot for this system showing the variation of freezing point with composition is represented in Figure 3.

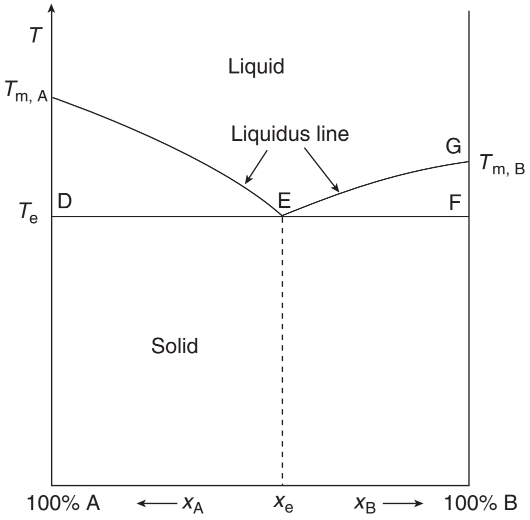


Figure 3 Solid–liquid equilibria in two-component system.

The points and curves represented in the figure are defined as follows:

1. **Liquidus curve:** The points above curve AE (or EG) represent liquid state of the system and this curve is called the liquidus curve. The points below this curve represents state in which pure solid coexists in equilibrium with solution.
2. **Eutectic temperature and composition:** We can see that for pure substance A, the freezing point is higher and upon increasing the concentration of B, the freezing point decreases to a lowest value. This is called the eutectic temperature, and the composition at this state is called **eutectic composition** (x_e).
3. **Eutectic point:** Point E represents the eutectic point in the Figure 3. The *eutectic* (Greek: easily melted) point is defined as the lowest meting point attained by the mixture. The longest eutectic halt gives the location of the eutectic composition and its melting temperature.

A point on EF represents pure solid B in equilibrium with solution of composition x_e, and a point on DE represents pure solid A in equilibrium with solution of composition x_e. Below the line DEF are the states of the system in which only the two solids, two phases, pure A and pure B, are present. The solution having the eutectic composition is in equilibrium with solid A and solid B both. Applying the reduced phase rule, the degree of freedom at eutectic point is:

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

Hence the system is invariant at this point. If heat flows out of the system, the temperature remains the same until one phase disappears and the amount of liquid diminishes while the amount of the two solids present increases.

Eutectic System

A two-component system in which both the components are completely miscible in liquid phase but do not react chemically is called a eutectic system.

Cd–Bi System

The cadmium–bismuth system is a simple eutectic system which exhibits no solubility of cadmium in bismuth or of bismuth in cadmium. Cadmium melts at 321°C and bismuth has a melting point of 271°C. Although they have no mutual solubility in solid state, they are completely miscible in the liquid state. The phase diagram for Cd–Bi system is shown in Figure 4.

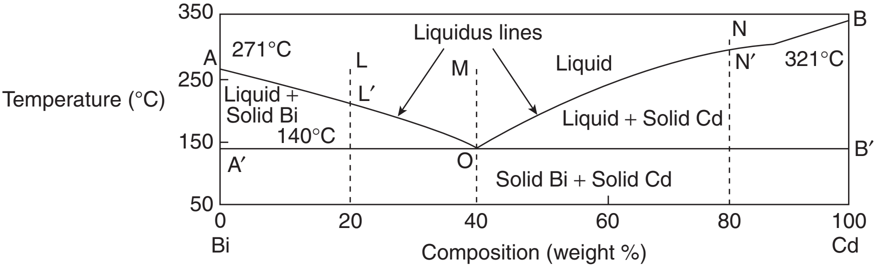


Figure 4 Phase diagram of Cd–Bi system.

It can be seen from the phase diagram that pure bismuth has high melting point (271°C) and addition of cadmium to liquid bismuth progressively decreases the freezing point to a lowest temperature of 140°C at 40% cadmium concentration (i.e., 40% Cd + 60% Bi). This is the eutectic point of the system. The eutectic point represents an invariant system and the three phases present in equilibrium are solid Bi, solid Cd and the liquid. The liquid phase cannot exist below this temperature.

If a liquid having composition and temperature corresponding to the point L is allowed to cool, it remains in the liquid phase till it reaches point L′ (at liquidus line). At this stage, small amount of Bi starts separating out, so that the remaining liquid becomes richer in Cd. On further cooling, solid Bi continuously gets separated out and the composition of the liquid changes along the liquidus line L′O until the eutectic point O is reached. When eutectic melt is allowed to cool, the temperature does not change until all the mass is solidified into a mixture of Cd and Bi having the eutectic composition.

Similarly, if a liquid having composition and temperature corresponding to the point M is allowed to cool, it remains in the liquid phase till it reaches the eutectic point O. On further cooling, it will solidify into a mixture of eutectic composition.

Likewise, if a liquid having composition and temperature corresponding to the point N is allowed to cool, it remains in the liquid phase till it reaches at point N′. On further cooling, solid Cd continuously gets separated out and the composition of the liquid changes along the liquidus line N′O till the eutectic point O is reached.

Eutectoid System

A eutectoid system describes the transformation of one solid into two different solids. For example, in iron–carbon system, austenite undergoes eutectoid transformation to produce ferrite and cementite (iron–carbide).

Fe–C system

Elemental iron exists in three crystallographic forms: α-iron, γ-iron and δ-iron. Molten iron freezes into the δ-iron (ferrite) at 1537°C. This phase has a body centered cubic (bcc) lattice and exists in equilibrium between 1537°C and 1404°C. The γ-iron has a face centered cubic (fcc) lattice and exists in equilibrium between 1404°C and 906°C. Below 906°C, the stable form of iron is α-iron which has a bcc lattice.

In the Fe–C system, one of the components (iron) is metal and the other is non-metal (carbon). The solid solutions of carbon in iron are interstitial solutions. The carbon atom fits in the space between iron atoms in the lattice without disturbing the crystal structure.

The various species present in the Fe–C system are:

1. **Austenite:** The maximum solubility of carbon in γ-iron is 1.7wt%. Austenite is not stable below 723°C.
2. **Ferrite:** It is the solid solution of carbon in α-iron. Carbon is only sparingly soluble in α-iron, the maximum solubility being 0.035wt% at 723°C. Therefore, ferrite is considered to be almost pure iron for practical purposes.
3. **Cementite:** It is the compound of carbon and iron having the formula Fe_3C. It is stable throughout the temperature range of the phase diagram.

The Fe–C phase diagram is represented in Figure 5.

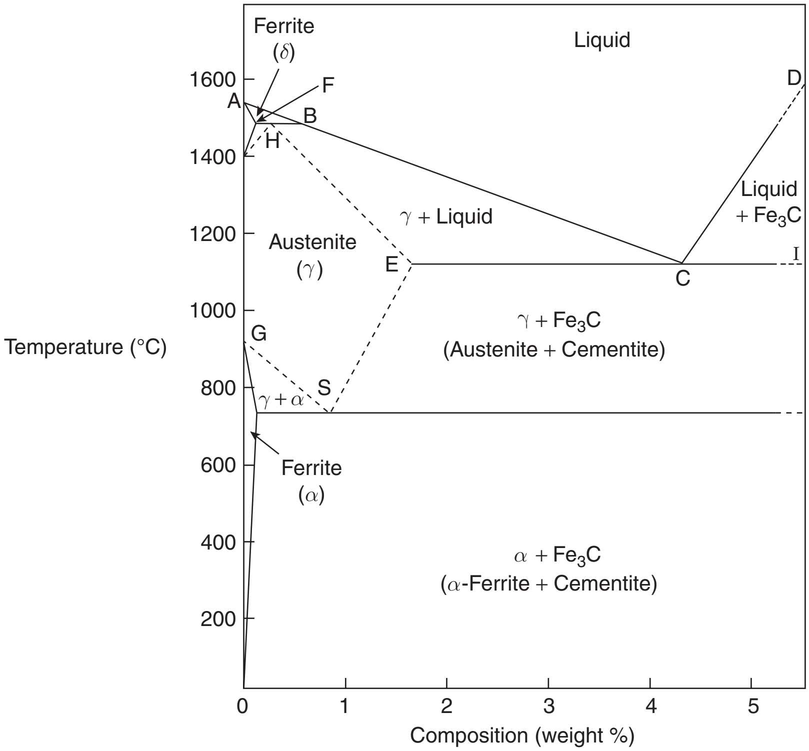


Figure 5 Fe–C phase diagram.

The various phases shown in the figure are described as follows:

1. The curve ABCD is the liquidus line and only liquid phase exists above this line.
2. The curve AFHECI is the solidus line and only solid phase exists below this line. The region between the solidus line and liquidus line represents a mixture of solid forms of iron and liquid.
3. When the liquid alloy of iron and carbon containing less than 0.55% carbon is cooled, a solid solution of carbon in δ-iron will crystallize out first. If the liquid alloys having 0.55–4.35% carbon are cooled, then austenite will crystallize out. When liquid alloys containing more than 4.3% carbon are cooled, crystallization of cementite (Fe_3C) starts.
4. It can be seen from the phase diagram that when carbon content is increased, the freezing point of alloy is continuously decreased until the eutectic composition is reached at 4.3 wt% carbon, the eutectic temperature being 1130°C. If the Fe–C alloy of eutectic composition (4.3 wt% C) is cooled it will completely solidify to give a solid eutectic mixture of austenite (γ-iron) and cementite (Fe_3C).

The Fe–C phase diagram is very helpful in understanding the various phase transformations that take place when liquid iron (containing carbon) is cooled. The Fe–C alloy having carbon content upto 1.7% is classified as steel and that having more than 1.7% carbon is called cast iron.

Concept Check

- What is condensed phase rule? Give examples of a system to which it can be applied.
- Define eutectic point. What are its characteristics?
- What is a eutectic system? Give two examples.
- What is meant by a eutectoid system? Give examples.

Key Terms

Phase
Component
Degree of freedom
Phase rule
Phase diagram
Stable phase
Metastable state
Clausius–Clapeyron equation
Triple point
Water system
Sulphur system
Solid–liquid equilibria
Eutectic point
Eutectic system
Bismuth–cadmium alloy
Vapor pressure curve
Freezing point curve
Eutectoid system
Iron–carbon system

Objective-Type Questions

Multiple-Choice Questions

1. Which of the following is a two-phase system?
   a. Water and ether
   b. Sand in water
   c. Kerosene in water
   d. All of the above.

2. For the reaction $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$, the number of phases are
   a. four.
   b. three.
   c. two.
   d. one.
3. How many phases are present in a saturated salt solution?
   a. One
   b. Two
   c. Three
   d. None of the above.
4. If two immiscible liquids are mixed together to form a solution, the number of phases would be
   a. two.
   b. three.
   c. four.
   d. one.
5. The dissociation of ammonium chloride in a closed vessel $NH_4Cl(s) \rightleftharpoons NH_4Cl(g) \rightleftharpoons NH_3(g) + HCl(g)$ is a
   a. one-component system.
   b. two-component system.
   c. three-component system.
   d. four-component system.
6. Gibbs phase rule is given by
   a. $F - P = C + 2$
   b. $F + P = C + 2$
   c. $F - C = P + 2$
   d. $P + C = F + 2$
7. At the triple point of a water system, the system is
   a. invariant.
   b. univariant.
   c. bivariant.
   d. none of the above.
8. The system of saturated salt solution is:

$$NaCl(s) \rightleftharpoons NaCl - water(aq \rightleftharpoons Water\ vapor(g)$$

   a. bivariant.
   b. invariant.
   c. univariant.
   d. trivariant.
9. In the phase diagram of water, the melting curve is almost a straight line which slopes backwards. If the pressure is increased, the melting point of ice will
   a. increase.
   b. decrease.
   c. increase up to a point and then decrease.
   d. remain the same.
10. The number of triple points in the phase diagram of sulphur (excluding the metastable triple point) are
    a. one.
    b. two.
    c. three.
    d. four.
11. The solid–liquid equilibrium at atmospheric pressure is best represented by
    a. pressure–temperature diagram.
    b. pressure–concentration diagram.
    c. temperature–concentration diagram.
    d. none of the above.
12. The modified phase rule equation for condensed system is
    a. $F = C - P + 1$
    b. $C = F - P + 1$
    c. $P + F = C + 2$
    d. $C = F - P + 2$
13. The condensed phase rule is applicable for
    a. a water system.
    b. a sulphur system.
    c. a Bi–Cd system.
    d. none of the above.
14. Which of the following is not true for eutectic point?
    a. Two solids and a liquid are in equilibrium at eutectic point.
    b. All melting points are eutectic points.
    c. All eutectic points are triple points.
    d. All of the above.

15. In a Bi–Cd system, the composition at the eutectic point is
    a. 60% Bi and 40% Cd.
    b. 70% Bi and 30% Cd.
    c. 4% Bi and 96% Cd.
    d. 2.4% Bi and 97.6% Cd.

Review Questions

Short-Answer Questions

1. Define a phase. Give examples of one- and two-phase systems.
2. What is the number of phases present in the following systems?
    a. A gaseous mixture of N_2, H_2 and NH_3 in equilibrium.
    b. A solution of two miscible liquids.
    c. A solution of two immiscible liquids.
    d. An emulsion of oil in water.
3. Determine the number of phases present in the following systems:
    a. saturated solution of NaCl.
    b. mixture of rhombic sulphur and monoclinic sulphur.
    c. Mixture of N_2 and O_2
    d. Mixture of CCl_4 and water.
4. What is meant by the term component?
5. How many components are present in the following systems?
    a. Water $\rightleftharpoons$ Water vapor
    b. $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$
    c. $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2$

       (in a closed vessel)
    d. $NaCl(s) \rightleftharpoons NaCl(aq)$
6. Determine the number of components in the following equilibria:
    a. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
    b. $PCl_5(s) \rightleftharpoons PCl_3(s) + Cl_2(g)$
    c. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
    d. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

       when $p_{NH_3} = p_{HCl}$
    e. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

       when $p_{NH_3} \neq p_{HCl}$
7. Explain why KCl–NaCl–H_2O should be regarded as a three-component system, whereas KCl–NaBr–H_2O should be regarded as a four-component system.
8. Explain that NH_4Cl in equilibrium with its dissociation products in a closed vessel is a one-component system.
9. What is meant by the term degree of freedom?
10. Calculate the degree of freedom of the following systems:
    a. $I_2(s) \rightleftharpoons I_2(g)$
    b. $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$
    c. $NaCl(s) \rightleftharpoons NaCl - \text{water(aq)}$

       $\rightleftharpoons \text{Water vapor(g)}$
11. What is the degree of freedom in the following systems? Name the variables corresponding to these degrees of freedom.
    a. Water(l) $\rightleftharpoons$ Water vapor(g)
    b. Water(l) $\rightleftharpoons$ Water vapor (at 1 atm)
12. State the phase rule and express it mathematically. Explain the terms involved in it.
13. What is the significance of Gibbs phase rule? What are its applications?
14. List two limitations of the phase rule.
15. State Clapeyron equation for phase transition from solid to liquid and liquid to vapor.
16. Define triple point. What is the triple point of water system?
17. For a one-component system, triple point is invariant. Explain.

18. In the phase diagram of ice, the fusion curve of ice has a negative slope whereas the sublimation curve has a positive slope. Explain.
19. Explain how, in principle, is it possible to convert solid ice into water vapor.
20. Explain the term metastable state.
21. Calculate the number of phases, components and degrees of freedom for the sulphur system.
22. What is the condensed phase rule? Where it is applied?
23. A eutectic mixture has a definite composition and a sharp melting point, yet it is not a compound. Explain.
24. Distinguish between congruent and incongruent melting points.
25. Distinguish between eutectic and eutectoid systems.
26. What is the temperature and composition at the eutectic point in Cd–Bi system?
27. What is the eutectoid transformation taking place in the iron–carbon system?

Long-Answer Questions

1. State Gibbs phase rule and define the terms (a) phase, (b) component and (c) degree of freedom.
2. **a.** Derive the Gibbs phase rule equation.
   b. What are the advantages of the phase rule?
3. Draw and label the phase diagram for water system. Explain the significance of areas, curves and triple point.
4. In the phase diagram for water system explain the following:
   a. invariant system,
   b. univariant system and
   c. bivariant system.
5. Discuss the application of phase rule to the sulphur system. Draw a labeled diagram.
6. What are the differences between phase diagrams of one- and two-component systems? State and explain the phase rule modified for condensed systems.
7. Draw a schematic phase diagram of the different phases (solid, liquid and vapor) of a substance.
8. Derive the Clausius–Clapeyron equation and discuss its significance.
9. **a.** Define eutectic mixture and eutectic point.
   b. Distinguish between triple point and eutectic point.
10. Draw and explain the phase diagram for a two-component system (Cd–Bi) not miscible in solid state and forming a simple eutectic mixture.
11. Discuss the application of phase rule to study a two-component system of solids, forming a compound with congruent melting point.
12. Draw and describe the phase diagram for a two-component system (Fe–C) undergoing a eutectoid reaction (transformation).

Answers

Multiple-Choice Questions

1. (d)
2. (b)
3. (c)
4. (b)
5. (a)
6. (b)

7. (a)
8. (c)
9. (b)
10. (c)
11. (c)
12. (a)
13. (c)
14. (b)
15. (a)

7

Reaction Kinetics and Catalysis

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Rate of the reaction and measurement of rates of reactions.
- Factors influencing rate of reaction.
- Rate laws and rate constants
- Order and molecularity of a reaction and the differences between them.
- Derivation of integrated reaction rates for first and higher order reactions.
- Half-lives of reactions.
- Pseudo-order reactions.
- Concept of activation energy.
- Arrhenius theory of temperature dependence of reaction rates.
- Theories of reaction rates.
- Catalysis – homogeneous catalysis, heterogeneous catalysis, autocatalysis, induced catalysis, acid–base catalysis and enzyme catalysis.

Chemical reactions are identified by the change in concentrations of reactants or products which is manifested by (a) direct methods through processes such as progressive de-colorization of reactants, formation of color, precipitation of products or gaseous evolution or (b) by indirect methods. These changes occur with different rates.

1. Many reactions are instantaneous such as photosensitivity of silver salts, precipitation of silver chloride on addition of an aqueous solution of silver nitrate to sodium chloride solution and explosive action of explosive materials.
2. Some reactions are very slow and may take place in months, or even a year or so. Even though hydrogen and oxygen are in contact with each other, water formation cannot be detected. This does not mean that they do not undergo reaction. In fact, they are reacting with each other so slowly that the product cannot be identified in appreciable time.
3. There are some moderately fast reactions whose rate can be found experimentally in reasonable time. Many gaseous reactions and reactions involving both organic and inorganic reactants come under this category.

To understand the path of the reactions, reactions should be moderately slow so that their intermediates can be isolated and characterized, and the mechanism of the reaction can be elucidated. This type of study on rate of chemical reactions is the scope of chemical kinetics. Thus, we can define **chemical kinetics** as follows:

Chemical kinetics deals with the study of the rate of chemical reactions and with the elucidation of the mechanisms by which they proceed.

7.1 Rate of Reaction

Measurement of Rate of Reaction

Rate or velocity of chemical reaction can be defined as the rate of formation of one or more of its products, or as the rate of consumption of one or more of its reactants. As the reaction proceeds, the concentration of reactants decreases and the concentration of products increases as shown in Figure 1.

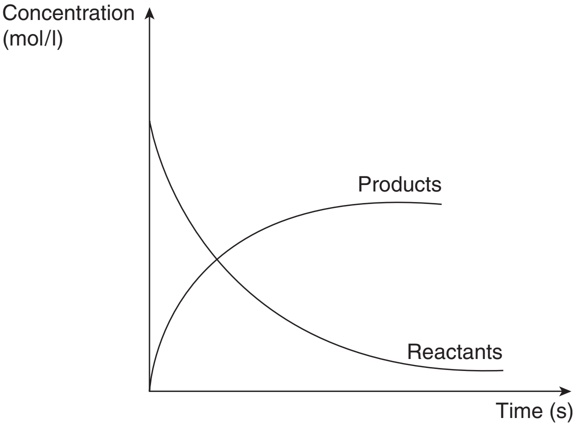


Figure 1 Variation of concentration with time.

For a general reaction,

$$aA + bB \rightarrow mM + nN$$

The rate of reaction may be defined by

$$-\frac{1}{a}\left(\frac{d[A]}{dt}\right) = -\frac{1}{b}\left(\frac{d[B]}{dt}\right) = +\frac{1}{m}\left(\frac{d[M]}{dt}\right) = +\frac{1}{n}\left(\frac{d[N]}{dt}\right)$$

where [A], [B], [M], [N] indicate the concentrations of A, B, M and N, respectively. The negative sign indicates that concentration of reactants falls as the reaction proceeds.

From an experimental point of view, if one wished to measure the rate of such a reaction, the same result would be obtained whether one measures the decrease in concentration of A (or B) or the increase in concentration of M (or N). Out of these, whichever method is easier to perform in the laboratory is chosen.

Any measurable change that takes place during a reaction may be used to determine reaction rates. For instance, if a reaction produces a colored substance, that is, one that has an absorption maximum at some wavelength in the visible spectrum, the increase in the absorbance of the solution in which the reaction takes place can be measured as a function of time. The absorbance of solute is directly proportional to the molar concentration and thus its measure is an easy way for determining the concentration and hence the rate. If the reaction involves gradual formation of a precipitate, the solution becomes progressively opaque with time. For such a reaction, rate can be measured by measuring the opacity. Similarly, for a reaction which involves evolution of gas,

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

the volume of hydrogen evolved can be measured at regular intervals of time, using which the rate of the reaction can be determined.

Factors Influencing Rate of Reaction

1. **Nature of the reactants:** A chemical reaction involves collision of molecules resulting in the rearrangement of atoms between the reacting molecules to form products. Old bonds in the reactants are broken and new bonds are formed. Thus, the nature and the strength of the bonds in reactant molecules greatly influence the rate of its transformation into products. For example, oxidation of ferrous ion by permanganate ion in acidic medium takes place at room temperature, whereas oxidation of oxalic acid by permanganate ion in acidic medium takes place at a slightly elevated temperature. Though both reactions are of similar type, as oxalic acid requires more bonds to be broken, some heat energy is required for the reaction to proceed.
2. **Temperature:** Most of chemical reactions are accelerated by increase in temperature. For example, oxidation of iron or coal is very slow at ordinary temperatures, but proceeds more rapidly at higher temperatures. In most cases, the rate of a reaction in a homogeneous reaction mixture is approximately doubled or even tripled by an increase in temperature of only 10°C. In some cases, this increase in reaction rate is even higher.
3. **Concentration of the reactants:** At a fixed temperature and in the absence of a catalyst, the rate of a given reaction increases with increase in concentration of reactants. When the concentration of the reactant is increased, the number of molecules per unit volume increases, thereby increasing the collision frequency, which ultimately causes the increase in reaction rate.
4. **Surface area of the reactants:** Finely divided reactants because of their larger surface area, react more rapidly than larger specimens of the same substance. For example, chips of wood burn faster than a log of wood.
5. **Catalysts:** Many reactions can be accelerated by the presence of small amount of substances, which themselves remain unaltered chemically during the course of reaction. Such substances are called catalysts. The action of the catalyst is specific for a reaction.
6. **Radiations**: A number of reactions register an increase in their rates, when radiations of specific wavelength are absorbed by the reacting molecules. Such reactions are called photochemical reactions. For example, a mixture of hydrogen and chlorine gases kept in the dark, if at all, reacts very slowly. An explosive reaction takes place when this mixture is subjected to a pulse of ultraviolet (UV) light.

$$\mathrm{H_2 + Cl_2 \rightarrow 2HCl}$$

Rate Laws

The rate of a chemical reaction is the rate at which the concentrations of interacting substances vary with time. The minus sign denotes that the concentration decreases. The dependence of this rate on the concentration of reacting substances is given by the law of mass of action. In general, if dx represents an infinitesimally small change in concentration of any species during the reaction time dt, then rate may be expressed as

$$\text{Rate} = \frac{\mathrm{d}x}{\mathrm{d}t}$$

The value of d*x*/d*t* may be obtained experimentally by plotting concentration of reactant (or product) against time. The mathematical expression that relates the rate of reaction to the concentration of either reactants or products is known as the rate law.

The rate of any reaction is at each instant proportional to the concentrations of the reactants, with each concentration raised to a power equal to the number of moles of each species participating in the reaction. Thus for the reaction, A → Products, the rate $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t$ should be proportional to [A],or

$$-\frac{\mathrm{dA}}{\mathrm{d}t} = k[\mathrm{A}] \tag{7.1}$$

where k is the constant of proportionality. For the reaction, 2A → Products, the rate $-\mathrm{d}\,[\mathrm{A}]/\mathrm{d}t$ should be proportional to $[\mathrm{A}]^2$, or

$$-\frac{\mathrm{dA}}{\mathrm{d}t} = k[\mathrm{A}]^2 \tag{7.2}$$

and for the reaction A + B → Products, the rate $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t$ should be proportional to [A][B],or

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}] \tag{7.3}$$

Similarly, for a reaction $a\mathrm{A} + b\mathrm{B} \rightarrow$ Products, the rate of the reaction is expressed as

$$\text{Rate} = k[\mathrm{A}]^a[\mathrm{B}]^b \tag{7.4}$$

The expression in Eqs. (7.1)–(7.4) which relates the rate of reaction to the concentration of the reactants is called **rate law**.

Concept Check

- Write the differential rate equation for the following reactions:
  - **a.** $\mathrm{A} + 2\mathrm{B} \rightarrow 2\mathrm{C} + \mathrm{D}$
  - **b.** $a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \rightarrow l\mathrm{L} + m\mathrm{M} + p\mathrm{P}$
- For a reaction, $\mathrm{A} + 2\mathrm{B} \rightarrow 3\mathrm{C}$, what is the rate formation of C?
- What do you understand from the term "rate of reaction"?
- How does temperature affect the rate of reaction?
- Give a suitable illustration for showing the influence of nature of the reactant on the rate of reaction.

7.2 Order and Molecularity

Order

Order of a reaction is an important parameter of a reaction which is always determined experimentally. It is defined as the total number of reactants whose concentration changes during the course of the reaction.

While considering a reaction, A → Products, suppose the rate of the reaction is (a) doubled when [A] is doubled, (b) tripled when [A] is tripled and (c) quartered when [A] is quartered; then the rate of the above reaction is proportional to first power of [A], that is

$$\text{Rate} \propto [\text{A}]$$

Suppose the rate of the above reaction is proportional to $[\text{A}]^2$, then (a) when [A] is doubled, the rate of the reaction would increase four times and (b) when [A] is tripled, the rate would increase nine times. Hence, the reaction rate is dependent on the power of the concentration terms involved in rate equation, which is called the **order** of the reaction.

If a reaction involves two or more reactants, then the rate of the reaction would be dependent on the power of concentration terms of individual reactants, and the order would be the algebraic sum of individual power terms. For a reaction between A and B, it can be experimentally determined that the rate of the reaction relates to the concentrations of A and B as follows:

$$\text{Rate} = k[\text{A}]^a[\text{B}]^b$$

where rate is the reaction rate in mol/l/s; k is the rate constant; [A] and [B] are concentrations in mol/l of reactants A and B, respectively; a is the order with respect to A and b is the order with respect to B. This is called the **rate equation** for the reaction. Following examples illustrate the order of the reaction:

1. $2\text{N}_2\text{O}_5 \rightarrow 4\ \text{NO}_2 + \text{O}_2$

$$\text{Rate} = k[\text{N}_2\text{O}_5] \tag{7.5}$$

The order of reaction is 1.

2. $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$

$$\text{Rate} = k[\text{H}_2][\text{I}_2] \tag{7.6}$$

The order of reaction is 1 + 1 = 2.

3. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2] \tag{7.7}$$

The order of reaction is 2 + 1 = 3.

Based on the algebraic sum of the powers of the concentration of the reactants, reactions may be classified as first-order, second-order, third-order, etc. There are certain reactions in which concentration of the reactant does not affect the reaction rate. Such reactions are called **zero-order reactions**. For example, decomposition of HI on gold surface.

From the rate law, we have

$$\frac{\text{d}x}{\text{d}t} = k[\text{Concentration of reactant}]^n$$

where $\text{d}x/\text{d}t$ is the rate of reaction, k is constant of proportionality and n is nth order of the reaction. Therefore,

$$k = \frac{\text{d}x}{\text{d}t} \times \frac{1}{[\text{Concentration}]^n} \tag{7.8}$$

Substituting the different values of n, we can calculate units of k for zero-, first-, second- and third-order reactions, which is illustrated as follows:

1. **Zero-order reaction:** Here $n = 0$,

$$k = \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) \times \frac{1}{[\text{Concentration}]^0} = \text{l/mol/time}$$

2. **First-order reaction:** Here $n = 1$,

$$k = \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) \times \frac{1}{[\text{Concentration}]^1} = \frac{\text{mol/l}}{\text{time}} \times \frac{1}{\text{mol/l}} = \text{time}^{-1}$$

3. **Second-order reaction:** Here $n = 2$,

$$k = \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) \times \frac{1}{[\text{Concentration}]^2} = \frac{\text{mol/l}}{\text{time}} \times \frac{1}{(\text{mol/l})^2} = \text{l/mol/time}$$

Molecularity

Molecularity is another factor useful for classifying the reactions. The molecularity of a reaction is defined as the total number of molecules of the reactants taking part in the step leading to a reaction, called rate determining step of a reaction. In other words, molecularity represents the number of reactant molecules undergoing collisions to bring about the chemical reaction. Thus in the reaction,

$$a\text{A} + b\text{B} \rightarrow \text{Products}$$

molecularity $= a + b$. The molecularity may be 1, 2, 3, etc. accordingly with the participation of one, two or three reactant molecules in the reaction. Depending upon this value, the reactions are classified as follows:

1. **Unimolecular reactions:** These reactions have molecularity 1. For example,

$$F_2O_2 \rightarrow F_2 + O_2$$

2. **Bimolecular reactions:** These reactions have molecularity 2. For example,

$$2HI \rightarrow H_2 + I_2$$

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

3. **Termolecular reactions:** These reactions have molecularity 3. For example,

$$2NO + Cl_2 \rightarrow 2\,NOCl$$

$$2NO + O_2 \rightarrow 2NO_2$$

The differences between order and molecularity are summarized in Table 1.

Table 1 Differences between order and molecularity

Order	*Molecularity*
Order of any reaction is the number of atoms or molecules which determine the rate of the reaction	Molecularity of any reaction is the number of atoms or molecules which take part in the rate determining step
It may be an integer, fraction or zero	It is always an integer

(*Continued*)

Table 1 Continued

Order	*Molecularity*
It is an experimental quantity and varies with the conditions of the reaction	It is a theoretical quantity that can be determined from the balanced chemical equation
It does not give any clue about the mechanism of the reaction	It gives information about the slowest step and hence helps in deriving the mechanism of the reaction

Concept Check

- What is a rate law? What is a rate constant?
- What is the order of a reaction? Do all rate laws have a reaction order?
- Derive the units of rate constant (k) of a second-order reaction.
- What are the differences between order and molecularity?
- What is the rate determining step of a reaction? What is its significance?

7.3 Integrated Rate Equations and Half-Lives

Zero-Order Reactions

In zero-order reactions, the rate is independent of the concentration of the reactants. Consider a zero-order reaction of the type A → Products. Let a be the initial concentration of the reactant and x be the concentration that is consumed at time t. Then the concentration of the reactant left at t is $a - x$. The rate equation is therefore,

$$\frac{dx}{dt} = k(a-x)^0 = k$$

On integration, it gives $k = x/t$ where k is the rate constant. The unit of rate constant is mol/l/s. In zero-order reaction, the rate constant is equal to the rate of reaction at all concentrations.

First-Order Reactions

Those reactions whose rate is determined by the change of only one concentration term are known as first-order reactions. Such reactions are represented by the following general reaction:

$$\text{A} \rightarrow \text{Products}$$

$$\text{Rate} = \frac{dx}{dt} = -\frac{d[A]}{dt} = k[\text{A}] \tag{7.9}$$

where k, a proportionality constant, is called the velocity constant, rate constant or specific rate constant. It is defined as the fraction of A that reacts per unit time. Taking [A] = 1 in Eq. (7.9), we find that the rate of the reaction is constant.

To deduce the integrated form of Eq. (7.9), it is convenient to put it in alternate form. Let us consider the initial concentration of A as a and the change in concentration of A due to reaction up to time t as $a - x$.

Therefore,

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{-\mathrm{d}(a-x)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}$$

and Eq. (7.9) becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-x) \tag{7.10}$$

This equation gives the rate for a first-order reaction in terms of initial concentration and the amount of substance reacted. On integration of Eq. (7.10) within the limits $x = 0$ when $t = 0$ and $x = x$ at $t = t$, we get

$$\int_{x=0}^{x=x} \frac{\mathrm{d}x}{a-x} = \int_{t=0}^{t=t} k\,\mathrm{d}t$$

$$\left[-\ln(a-x)\right]_{x=0}^{x=x} = [kt]_{t=0}^{t=t}$$

$$\ln\frac{a}{a-x} = kt \tag{7.11}$$

Rate constant for a first-order reaction,

$$k = \frac{1}{t}\ln\left(\frac{a}{a-x}\right)$$

where a is the initial concentration of A, and x is the concentration of A reacted after time t. The quantity $a/(a–x)$ is dimensionless, so the unit of k is time^{-1}. Any first-order reaction should satisfy Eq. (7.11).

Half-life period: It is the time taken for the completion of half of the reaction. That is, if $x = a/2$ at $t = t_{1/2}$, then, from Eq. (7.11) it can be deduced that

$$t_{1/2} = \frac{0.693}{k}$$

Thus, the half-life period for a first-order reaction is constant and independent of initial concentration of the reacting species.Some examples of first-order reactions include dissociation of nitrous oxide, nitrogen pentoxide, acetone and hydrogen peroxide.

To find whether a particular reaction obeys this equation, a few methods are available:

1. Knowing the initial concentration and the concentrations of reactant at various intervals of time, a, $(a - x)$ and t may be substituted in the equation and k can be found. If constancy within the accuracy of the experiment is found, the reaction is ascertained to obey first order.
2. Equation (7.11) can be tested by plotting a graph of log $(a - x)$ vs. t in the modified equation of Eq. (7.11) as

$$\ln(a-x) = -kt + \ln a$$

$$\log_{10}(a-x)=\frac{-k}{2.303}t+\log_{10}a \tag{7.12}$$

If the plot yields a straight line with the intercept $\log_{10} a$ and the slope $-k/2.303$, then the reaction is of first order.

3. Using half-life period, it can be found out whether the reaction is of first order or not.

Second-Order Reactions

Reactions in which rate is determined by changing two concentration terms are known as second-order reactions. These reactions may be of two types:

1. **When two molecules of the same reactant are involved in the reaction:** The rate is determined by the two concentration terms of the same molecule. Such a reaction is generalized as 2A → Products. In such types of reactions, the rate of reaction is

$$-\frac{d[A]}{dt}=k[A]^2$$

where [A] is the concentration of reactant A. One typical example is the decomposition of hydrogen iodide,

$$2HI \rightarrow H_2 + I_2$$

Let the initial concentration of the two molecules of A be in moles per unit volume, respectively, and after a time lapse t, let x moles of each be converted into products. This means that the concentrations remaining will be $a-x$ moles per unit volume, respectively. Then the rate equation is modified as

$$-\frac{d[A]^2}{dt}=-\frac{d(a-x)^2}{dt}=\frac{dx}{dt}=k(a-x)^2 \tag{7.13}$$

Integrating Eq. (7.13), we get

$$\int\frac{dx}{(a-x)^2}=\int k\,dt$$

$$\left\{\frac{1}{a-x}\right\}=kt+c \tag{7.14}$$

where c is the constant of integration. It can be eliminated by substituting $x=0$ when $t=0$ in Eq. (7.14). The equation simplifies to

$$\left\{\frac{1}{a-x}\right\}=kt+\frac{1}{a}$$

$$k=\frac{1}{at}\left\{\frac{x}{a-x}\right\} \tag{7.15}$$

Rate constant of second-order reactions having only one reactant, is given by

$$k = \frac{1}{t}\left\{\frac{x}{a(a-x)}\right\} \tag{7.16}$$

The quantity $x/(a-x)$ is dimensionless, so units of k are $(\text{concentration})^{-1}$ time^{-1}, that is, l/mol/time.

Half-life period: It is given by $t_{1/2} = 1/ka$. Hence $t_{1/2}$ of second-order reaction is inversely proportional to the initial concentration of reactant.

2. **When two different reactants of different concentrations are involved in a reaction:** The rate is determined by the change of two concentration terms of two different reactants. Such a reaction is generalized as A + B $\rightarrow$ Products. The rate of reaction is,

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}] \tag{7.17}$$

where [A] and [B] are the concentration of reactants A and B, respectively, at any given time t, and k is the velocity constant. For example,

$$\mathrm{CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH}$$

Let the initial concentration of A and B be a and b moles per unit volume, respectively, and after a time lapse t, let x moles of each be converted into products. This means that the concentrations remaining will be $a-x$ and $b-x$ moles per unit volume, respectively. Then the rate equation can be written as

$$-\frac{\mathrm{d}(a-x)}{\mathrm{d}t} = -\frac{\mathrm{d}(b-x)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t}$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-x)(b-x)$$

Integrating, we get

$$\int \frac{\mathrm{d}x}{(a-x)(b-x)} = \int k\,\mathrm{d}t$$

$$\left\{\frac{1}{a-b}\right\}\int\left[\frac{1}{a-x} - \frac{1}{b-x}\right]\mathrm{d}x = kt + c$$

$$\left\{\frac{1}{a-b}\right\}[\ln(a-x) - \ln(b-x)] = kt + c \tag{7.18}$$

At the beginning of the reaction, the change in concentration of the reactants is zero. That is, at $t = 0$, $x = 0$. Applying this to Eq. (7.18), the equation becomes

$$\frac{1}{a-b}[\ln(a) - \ln(b)] = c \tag{7.19}$$

On substitution of c using Eq. (7.19) in Eq. (7.18) and on rearrangement, Eq. (7.18) becomes

$$\frac{1}{a-b}[\ln(a-x) - \ln(b-x)] = kt + \left(\frac{1}{a-b}\right)[\ln a - \ln b]$$

$$\frac{1}{a-b}[\ln(a-x)-\ln(b-x)]-\left(\frac{1}{a-b}\right)[\ln a-\ln b]=kt$$

$$\frac{1}{a-b}\ln\left(\frac{b(a-x)}{a(b-x)}\right)=kt \tag{7.20}$$

$$k=\frac{1}{t(a-b)}\ln\left(\frac{b(a-x)}{a(b-x)}\right) \tag{7.21}$$

Therefore, the rate constant of second-order reactions having two different reactants is

$$k=\frac{1}{t}\left(\frac{2.303}{a-b}\right)\log\left(\frac{b(a-x)}{a(b-x)}\right) \tag{7.22}$$

The units of rate constant are (1/time) × (1/mol/l) × [(mol/l)(mol/l)/(mol/l)(mol/l)] = l/mol-time, that is, Eqs. (7.16) and (7.22) may be tested by substitution of values of a, x and a, b and x along with t as described for first-order reactions. For the verification of second-order for reactions by graphical method, Eq. (7.22) can be written as

$$t=\left[\frac{2.303}{k(a-b)}\log_{10}\left\{\frac{(a-x)}{(b-x)}\right\}\right]+\left[\left\{\frac{2.303}{k(a-b)}\right\}\log_{10}\left(\frac{b}{a}\right)\right] \tag{7.23}$$

A plot of t against $\log_{10}\{(a-x)/(b-x)\}$ should form a straight line with slope $\{2.303/k(a-b)\}$ and the intercept in y-axis,

$$\frac{2.303}{k(a-b)}\log_{10}\left(\frac{b}{a}\right)$$

The examples of second-order reactions are as follows:

1. **Gas phase reactions:** Thermal dissociation of oxygen, ozone, chlorine monoxide, nitrous oxide, etc.
2. **Solution phase reactions:** These include saponification of ester. Hydrolysis of an ester by an alkali is known as saponification of ester,

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

The hydroxyl ions act as catalyst, but are used up because they react with the acetic acid produced by the reaction. If the alkali used is caustic soda, the product will be sodium acetate and ethanol, and the rate of reaction will be:

$$\text{Rate} = k[\,CH_3COOC_2H_5][OH^-]$$

Some other important examples are as follows:

1. Condensation of benzaldehyde to benzoin.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{OH^-} \underset{\text{Benzoin}}{C_6H_5CH(OH)COC_6H_5}$$

2. Conversion of ammonium cyanate to urea

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \rightarrow \underset{\text{Urea}}{H_2NCONH_2}$$

Third-Order Reactions

A third-order reaction is one whose rate depends on the first power of concentration terms of three individual molecules involved in the reaction. The generalized reaction is A + B + C → Products. If the reactants are all present in different initial concentrations a, b, c and x is the decrease in the concentration of each reactant at time t, then the third-order rate equation is

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x) \tag{7.24}$$

The integrated form cannot be solved easily. However, a simpler case where two of the initial concentrations are equal, that is, $a = b$, changes Eq. (7.24) to

$$\frac{dx}{dt} = k(a-x)^2(c-x) \tag{7.25}$$

Integrating Eq. (7.25) gives

$$k = \left\{\frac{1}{t(c-a)^2}\right\}\left[\frac{x(c-a)}{a(a-x)} + \ln\left\{\frac{c(a-x)}{a(c-x)}\right\}\right] \tag{7.26}$$

Another case of a third-order reaction is 2A + B → Products, the concentrations at any time t are $(a-2x)$ and $(b-x)$. The rate equation becomes

$$\frac{dx}{dt} = k(a-2x)^2(b-x) \tag{7.27}$$

On integration,

$$k = \frac{1}{t(2b-a)^2}\left[\frac{2x(2b-a)}{a(a-2x)} + \ln\left\{\frac{b(a-2x)}{a(b-x)}\right\}\right] \tag{7.28}$$

There is yet another case, 3A → Products, where $a = b = c$, for which the rate equation can be written as,

$$\frac{dx}{dt} = k(a-x)^3 \tag{7.29}$$

Integrating Eq. (7.29), it gives

$$k = \frac{1}{2ta^2}\left\{\frac{x(2a-x)}{(a-x)^2}\right\} \tag{7.30}$$

The examples of third-order reactions are

1. $2NO + H_2 \rightarrow N_2O + H_2O$ (gaseous phase)
2. Oxidation of ferrous sulphate in water (solution phase).

Half-life period: Half- life of a third-order reaction can be deduced as $t_{1/2} = 3/2ka^2$. It is inversely proportional to a^2.

Higher nth Order Reactions

In general, a reaction whose order is n can be written as A ⟶ Products. Let a be the initial concentration of the reactant and x be the concentration that is consumed at time, t. Then the concentration of the reactant at t is $a–x$. The rate equation is therefore,

$$\frac{dx}{dt} = k(a-x)^n$$

$$\frac{dx}{(a-x)^n} = k\,dt$$

On integration, it gives,

$$\int \frac{dx}{(a-x)^n} = k\int dt$$

$$\frac{(a-x)^{n+1}}{-n+1} = kt + c$$

$$\frac{1}{(a-x)^{n-1}(n-1)} = kt + c$$

At $t = 0$, x is also equal to zero. Applying this in the above equation, it gives

$$\frac{1}{\{(a)^{n-1}(n-1)\}} = c$$

On substituting this in the above equation,

$$\frac{1}{(a-x)^{n-1}(n-1)} = kt + \frac{1}{(a)^{n-1}(n-1)}$$

$$kt = \frac{1}{(a-x)^{n-1}(n-1)} - \frac{1}{(a)^{n-1}(n-1)}$$

$$= \frac{1}{n-1}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

Half-life period: When $t = t_{1/2}$, $a = a/2$;

$$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{1}{\{a-(a/2)\}^{n-1}} - \frac{1}{a^{n-1}}\right]$$

$$= \frac{1}{k(n-1)}\left[\left(\frac{2}{a}\right)^{n-1} - \frac{1}{a^{n-1}}\right]$$

$$= \frac{1}{k(n-1)}\left(\frac{2^{n-1}-1}{a^{n-1}}\right)$$

In general, half-life of reaction of *n*th order is,

$$t_{1/2} \propto \frac{1}{a^{n-1}} \tag{7.31}$$

Problem 1

At 373 K, the half-life period for the thermal decomposition of N_2O_5 is 4.6 s and is independent of the initial pressure of N_2O_5. Calculate the specific rate constant at this temperature.

Solution

Since the half-life period is independent of the initial pressure, this shows that the reaction of the first order. For a reaction of the first order, we know that

$$k = \frac{0.693}{4.6} = 0.1507 \text{ s}^{-1}$$

Problem 2

A first-order reaction is 40% complete in 50 min. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

Solution

For the first-order reaction,

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$$

Given that when $x = (40/100)\ a = 0.4a$, $t = 50$ min, so

$$\begin{aligned} k &= \frac{2.303}{50}\log\left(\frac{a}{a-0.4a}\right) \\ &= \frac{2.303}{50}\log\left(\frac{1}{0.6}\right) = 0.010216 \text{ min}^{-1} \end{aligned}$$

Problem 3

At 373 K, a gaseous reaction $A \rightarrow 2B + C$ is observed to be of first order. On starting with pure A, it was found that at the end of 10 min the total pressure of the system was 176 mm of Hg; and after a long time, when dissociation of A was complete, it was 270 mm. Calculate

(a) the initial pressure of A.
(b) the pressure of A at end of 10 min.
(c) the rate constant.

Solution

Suppose initial pressure of A = p_1 mm.
Decrease in the pressure of A after time $t = p$ mm
Now, for the reaction A→2B + C, we have

Pressure	*A*	*2B*	*C*	*Total Pressure*
Initial	p_1	0	0	p_1
After time t	$p_1 - p$	$2p$	p	$p + 2p$
Final	0	$2p_1$	p_1	$3p_1$

(a) Given that final pressure = 270 mm Hg; therefore, $3p = 270$ or $p_1 = 90$ mm Hg.
(b) Given that pressure after 10 min = 176 mm Hg. Therefore,

$$p_1 + 2p = 176 \quad \text{or} \quad 90 + 2p = 176$$

or $p = 43$ mm Hg.
Pressure of A after 10 min = $p_1 - p = 90 - 43 = 47$ mm Hg.

(c) The initial concentration a is proportional to p_1 and the concentration at time t, that is, x is proportional to p. Therefore,

$$k = \frac{2.303}{t} \log\left(\frac{a}{a - x}\right) = \frac{2.303}{t} \log \frac{p_1}{p_1 - p}$$

or

$$k = \frac{2.303}{10} \log \frac{90}{(90 - 43)} = 6.496 \times 10^{-2}\ \text{min}^{-1}$$

Problem 4

Find the general expression for the time taken for nth fraction of a first-order reaction to complete.

Solution

Putting, $x = a/n$ and $t = t_{1/n}$ in the following first-order equation

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

we get

$$t_{1/n} = \frac{2.303}{k} \log \frac{a}{a - (a/n)} = \frac{2.303}{k} \log \frac{1}{1 - (1/n)}$$

or

$$t_{1/n} = \frac{2.303}{k} \log \frac{n}{n - 1}$$

Problem 5

A second-order reaction, where $a = b$, is 20% complete in 500 s. How long will it take for the reaction to go for 60% completion?

Solution

For a second-order reaction,

$$k_2 = \frac{1}{t} \times \frac{x}{a(a-x)}$$

When the reaction is 20% complete, x is 20% of the initial concentration a, that is,

$$20\% \text{ of } a = \frac{20a}{100} = 0.2a$$

So,

$$k_2 = \frac{1}{500} \times \frac{0.2a}{a(a-0.2a)} = \frac{1}{200a}$$

Now suppose it takes t_1 seconds for the reaction to go for 60% completion, then for 60% completion,

$$x = \frac{60a}{100} = 0.6a$$

Thus,

$$k_2 = \frac{1}{t} \times \frac{0.6a}{a(a-0.6a)}$$

$$\frac{1}{200a} = \frac{1}{t_1} \times \frac{3}{2a}$$

which gives $t_1 = 3000$ s.

Problem 6

For the reaction A + B → Products, the rate is given by the rate law equation:

$$\text{Rate} = k[\text{A}]^x [\text{B}]^y$$

Calculate the order of reaction and the rate constant from the following initial concentrations and corresponding rates.

{A} (in mol/l)	0.1	0.1	0.2
{B} (in mol/l)	0.2	0.4	0.2
Rate (mol/l/s)	3×10^3	12×10^3	6×10^3

Solution

Given that rate = $k[A]^x[B]^y$. Substituting for each value of concentration and rate:

$$R_1 = 3\times10^3\ \text{mol/l/s} = k(0.1\ \text{mol/l})^x \times (0.2\ \text{mol/l})^y$$

$$R_2 = 12\times10^3\ \text{mol/l/s} = k(0.1\ \text{mol/l})^x \times (0.4\ \text{mol/l})^y$$

$$R_3 = 6\times10^3\ \text{mol/l/s} = k(0.2\ \text{mol/l})^x \times (0.2\ \text{mol/l})^y$$

To find y, we divide R_1 by R_2 to obtain

$$\frac{R_1}{R_2} = \frac{3\times10^3}{12\times10^3} = \frac{k(0.1)^x \times (0.2)^y}{k(0.1)^x \times (0.4)^y}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^y$$

or $$y = 2$$

Therefore, the order of reaction with respect to B is 2. Similarly, to find x, we divide R_1 by R_3, to get

$$\frac{R_1}{R_3} = \frac{3\times10^3}{6\times10^3} = \frac{k(0.1)^x \times (0.2)^y}{k(0.2)^x \times (0.2)^y}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^x$$

or $$x = 1$$

Therefore, the order of reaction with respect to A is 1. The overall order of reaction is 3. The rate constant k for any concentration is given by

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

Substituting the values, we get

$$k = \frac{3\times10^3}{(0.1)\times(0.2)^2} = \frac{3\times10^3}{4\times10^{-3}} = 0.75\times10^6\ \text{l}^2/\text{mol}^2/\text{s}$$

Problem 7

For a first-order reaction, show that the time required for completion of 99.9% of reaction is about 10 times the time required for completion of half the reaction.

Solution

For a first-order reaction

$$t_{1/2} = \frac{0.693}{k} \tag{7.32}$$

where k is the reaction constant. The time required for 99.9% completion of reaction can be obtained from the equation:

$$t_{(99.9\%)} = \frac{2.303}{k} \log\frac{[A_0]}{[A]} \tag{7.33}$$

where $[A_0]$ is initial concentration and $[A]$ is final concentration at time $t_{(99.9)\%}$. $[A]$ can be found as

$$\begin{aligned}[A] &= [A_0] - 99.9\%[A_0] = [A_0] - \frac{99.9}{100}[A_0] \\ &= 0.1\times 10^{-2}[A_0] = 10^{-3}[A_0]\end{aligned}$$

Substituting for $[A]$ in Eq. (7.33), we get

$$t_{(99.9\%)} = \frac{2.303}{k} \log\frac{[A_0]}{10^{-3}[A_0]} \tag{7.34}$$

or $$t_{(99.9\%)} = \frac{2.303}{k} \log 1000 = \frac{2.303\times 3}{k} = \frac{6.909}{k} \quad (\text{as} \log 1000 = 3)$$

Dividing Eq. (7.34) by Eq. (7.32) we get

$$\frac{t_{(99.9\%)}}{t_{(50\%)}} = \frac{6.909}{k} \times \frac{k}{0.693} \approx 10$$

Problem 8

The rate constant for a first-order reaction is $3.2 \times 10^{-5}\ s^{-1}$ at a particular temperature. What percentage of reactants will react on heating for 1.5 h?

Solution

For first-order reaction,

$$k = \frac{2.303}{t} \log\frac{[A_0]}{[A]}$$

where $[A_0]$ is initial concentration and $[A]$ is concentration at time t. Given that $k = 3.2 \times 10^{-5}\ \text{s}^{-1}$ and $t = 3/2\ \text{h} = 5400\ \text{s}$. Substituting these in the equation, we get

$$3.2\times10^{-5} = \frac{2.303}{5400}\times\log\frac{[A_0]}{[A]}$$

$$\log\frac{[A_0]}{[A]} = \frac{3.2\times10^{-5}\times5.4\times10^{3}}{2.303} = 0.07503$$

$$\frac{[A_0]}{[A]} = 1.189$$

$$[A] = \frac{[A_0]}{1.189} = 0.8410[A_0]$$

Percentage of reactant left unreacted after heating for 1.5 h is 84.1%. Therefore, the percentage of reactant that has reacted is 15.9%.

Problem 9

The initial rate of a second-order reaction is 4×10^{-4} mol/l/s. If the initial concentration of the reacting substance is 0.20 mol/l, calculate the rate constant.

Solution

The second-order reaction may be represented as 2A → Products. The rate law equation is

$$\text{Rate} = k[A]^2$$

Given that the rate $= 4 \times 10^{-4}$ mol/l/s; concentration of reactant A = 0.20 mol/l. Substituting these values in the rate law equation, we get

$$4\times10^{-4} = k[0.20\times0.20]$$

Therefore, the rate constant is calculated as

$$k = \frac{4\times10^{-4}}{0.04} = 1\times10^{2}\ \text{l/mol/s}$$

Problem 10

In a second-order reaction, the reaction is found to be 25% complete in 30 min. The initial concentration of the reactant is 0.5 mol/l. Calculate the (a) rate constant, (b) half-life period and (c) time required for completion of 90% of the reaction.

Solution

(a) For a second-order reaction, $2A \longrightarrow$ Products, the integrated rate law equation is given by

$$kt = \frac{1}{[A]} - \frac{1}{[A_0]}$$

where $[A_0]$ is the initial concentration and $[A]$ is the concentration at time t. When the reaction is 25% complete

$$[A] = 75\%\ [A_0] = 0.75\ [A_0]$$

Given that $[A_0] = 0.5$ mol/l, therefore

$$[A] = 0.75 \times 0.5 = 0.375 \text{ mol/l}$$

Now, substituting $t = 30$ min in the integrated rate law equation, we get the rate constant as

$$k = \frac{1}{30} \times \left(\frac{1}{0.375} - \frac{1}{0.5} \right) = \frac{1}{30}(2.67 - 2) = 0.0223 \text{ l/mol/min}$$

(b) Half-life period for second-order reaction is given by

$$t_{1/2} = \frac{1}{k[A_0]}$$

Substituting the value of k, we get the half-life period as

$$t_{1/2} = \frac{1}{0.0223 \times 0.5} = 89.68 \text{ min}$$

(c) When the reaction is 90% complete

$$[A] = 10\%[A_0] = 0.1 \times [A_0]$$

Given that $[A_0] = 0.5$ mol/l. Therefore,

$$[A] = 0.5 \times 0.1 = 0.05 \text{ mol/l}$$

Substituting the values of k and $[A]$ in the expression for time period, we get

$$\begin{aligned} t &= \frac{1}{k}\left(\frac{1}{[A]} - \frac{1}{[A_0]} \right) \\ &= \frac{1}{0.0223}\left(\frac{1}{0.05} - \frac{1}{0.5} \right) \\ &= \frac{1}{0.0223}(20 - 2) = 807.12 \text{ min} \end{aligned}$$

Concept Check

- What is a zero-order reaction?
- For a zero-order reaction, how does the half-life period vary with concentration?

- Deduce the rate constant of a first-order reaction.
- Define half-life period. Show that half-life period of a first-order reaction is independent of concentration of the reactant.
- For a second-order reaction with two different reactants, half-life period cannot be determined. Why?
- What is the general expression relating rate constant of *n*th order reaction to its initial concentration *a*?
- Reactions of third and higher orders are usually not very common. Why?
- How does the half-life period of an *n*th order reaction vary with the initial concentration of the reactant?

7.4 Pseudo-Order Reactions

A reaction whose order is different from the actual order due to large excess concentration of one of the reactants is called **pseudo-order reaction**. Consider a reaction, A + B → Products in which the reactant B is present in large excess.
The rate equation can be written as

$$\text{Rate} = k[\text{A}][\text{B}]$$

As B is present in large excess, its concentration remains practically constant in the course of the reaction. Thus, the rate law can be written as

$$\text{Rate} = k'[\text{A}]$$

when the new rate constant $k' = k[\text{B}]$. Thus, the actual order of the reaction is second order but in practice it will be first-order. Hence, the reaction is said to have a pseudo-first-order reaction. Some examples of pseudo-order reactions are as follows:

1. **Hydrolysis of an ester:** Ethyl acetate on hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.

   $$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

   Here a large excess of water is used and the rate law can be written as

   $$\text{Rate} = k[CH_3COOH][H_2O] = k'[CH_3COOH]$$

   This reaction is actually a second-order reaction but in practice it is found to be first order. Hence, it is a pseudo-first-order reaction.
2. **Hydrolysis of sucrose:** Sucrose upon hydrolysis in the presence of a dilute mineral acid gives glucose and fructose.

   $$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

   If large excess of water is present, its concentration is practically constant and the rate may be written as

   $$\text{Rate} = k[C_{12}H_{22}O_{11}][H_2O] = k'[C_{12}H_{22}O_{11}]$$

   Though the actual order is 2, its experimental order is 1. Thus it is a pseudo-first-order reaction.

Concept Check

- For the reaction A + B → C + D, rate = $k[A]^2[B]^{1/2}$. Find the order when (a) A is present in large excess and (b) B is taken in large excess.
- A second-order reaction behaves as a first-order reaction when one of the reactants is present in large excess? Explain.

7.5 Temperature Dependence of Rate of Reactions

Temperature Coefficient

The rate of all single reactions increases with the increase in temperature. As such there is no general rule regarding the magnitude with which the rate of a reaction varies with temperature. But, a 10°C rise in temperature generally doubles or triples the reaction rate. The ratio of the velocity constants of a reaction at two temperatures separated by 10°C is known as **temperature coefficient**. The temperatures usually selected for this purpose are 25°C and 35°C. Thus mathematically,

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } 35^\circ\text{C}}{\text{Rate constant at } 25^\circ\text{C}} = \frac{k_{35^\circ\text{C}}}{k_{25^\circ\text{C}}}$$

Temperature coefficient is nearly 2 although in some cases it approaches even 3. For example, the temperature coefficients for dissociation of HI, and for the reaction between methyl iodide and sodium ethoxide are 1.8 and 2.9, respectively.

$$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$$

$$\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{ONa} \rightarrow \text{CH}_3\text{OC}_2\text{H}_5 + \text{NaI}$$

Further, greater the difference in temperature, greater will be the difference in reaction rates. For example, increase of 160°C in temperature during the decomposition of acetaldehyde increases the reaction rate 453 times.

Activation Energy

The increase in reaction rate with the increase in temperature is explained on the basis of collision theory. According to collision theory, although a reactant molecule collides with another reactant molecule a billion times per second, only those collisions which possess a certain minimum amount of energy result in chemical reaction. This minimum amount of energy which must be associated with molecules so that their mutual collisions result in chemical reaction is called **threshold energy (E_T).**

In a given sample of gas, all the molecules do not possess similar velocity and hence kinetic energy. In fact, at a given temperature there is a definite distribution of velocities or kinetic energies amongst the various molecules of gas. At low temperature (say T_1), only a small part of the molecules has very low kinetic energy. Another small part has very high kinetic energy and a larger part has intermediate kinetic energy. Further, as the temperature is increased, from T_1 to T_2, energy re-distribution takes place. More number of molecules acquire high kinetic energy (Figure 2). The excess energy acquired by the reacting molecules is known as activation energy (E_a), that is,

Activation energy = Threshold energy − Actual energy possessed by molecules energy

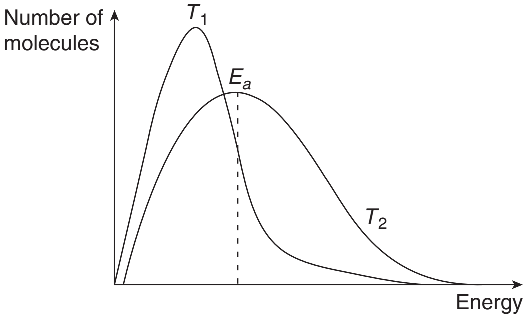


Figure 2 Energy distribution curve for a reaction at two different temperatures.

Thus according to activation energy concept, non-active molecules (having energy less than the threshold energy) can be activated by absorption of extra energy, known as the **activation energy**. In other words, the reactant species have to acquire a certain amount of energy before they can react to yield products, that is, there is an energy barrier which must be crossed over by the reactants to be converted into the products. This energy barrier determines the magnitude of threshold energy which reactant molecules must acquire before they can yield products (Figure 3).

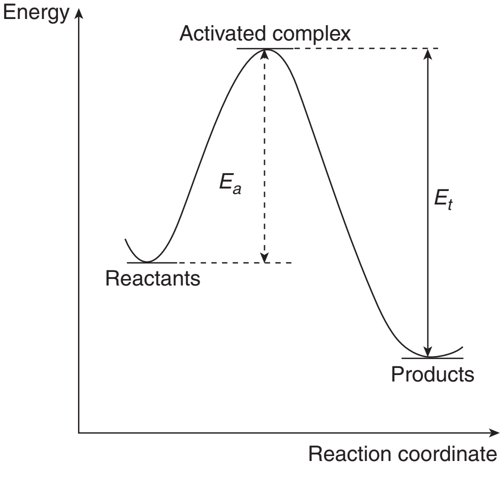


Figure 3 Energy barrier in chemical reactions.

When the energy of products is less than that of the reactants, the reaction is exothermic and thus ΔH will be negative (Figure 4a). The reaction is endothermic when energy of products is higher than that of reactants and ΔH is positive (Figure 4b).

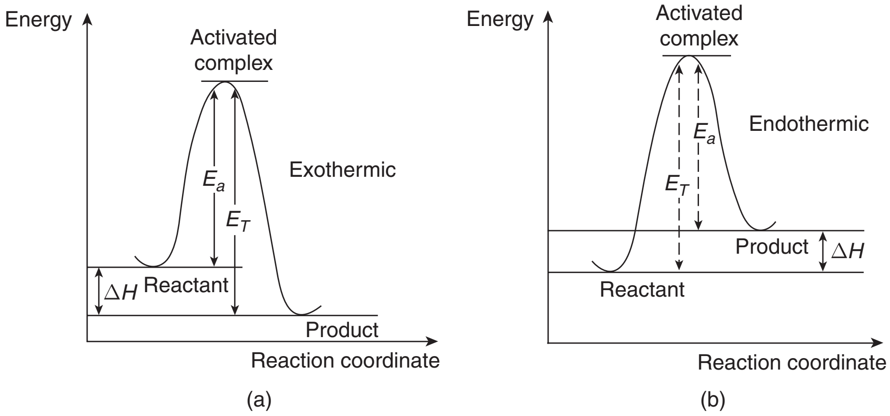


Figure 4 Energy profile for (a) Exothermic reaction, (b) endothermic reaction.

Different reactions have different amount of activation energy. A reaction which has higher activation energy is slow at ordinary temperatures, while the reaction having lower activation energy will proceed at a faster rate at a given temperature. Thus the difference in activation energy is mainly responsible for observed difference in rates of reactions.

Arrhenius Equation

The relationship between the rate of reaction and temperature is quantitatively expressed by Arrhenius equation. According to this equation, activation energy of a reaction with k as the rate constant and at temperature T may be given by the following empirical relation,

$$k = A \cdot e^{-E_a/RT} \tag{7.35}$$

where A is constant, known as frequency factor; E_a is activation energy of the reaction; R is gas constant and T is temperature on absolute scale. Taking the logarithmic form of Eq. (7.35), we get

$$\log_{10} k = \left(\frac{-E_a}{2.303R}\right)\frac{1}{T} + c \tag{7.36}$$

where c is integration constant. The values k_1 and k_2 of a reaction at temperatures T_1 and T_2 are related by the following relation:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{7.37}$$

Thus, activation energy can be evaluated by knowing the values of rate constants k_1 and k_2 at temperatures T_1 and T_2.

Alternatively, the value of E_a can be evaluated by plotting a graph (Figure 5) between log k and $1/T$. The graph will give a straight line whose slope is equal to $-E_a/2.303R$ or $-E_a/5.476$, from which the value of E_a can be determined.

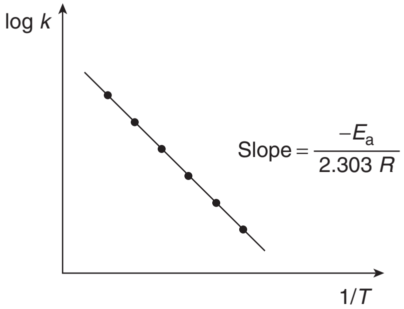


Figure 5 Arrhenius plot.

Problem 11

The rate constant of a reaction is $1.5 \times 10^7\ s^{-1}$ at 50°C and $4.5 \times 10^7\ s^{-1}$ at 100°C. Evaluate E_a. Given that $R = 8.314$ J/K/mol.

Solution

The Arrhenius equation is,

$$k = A\exp\left(\frac{E_a}{RT}\right)$$

For the two temperatures, we get

$$\log\frac{k_2}{k_1} = \frac{-E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substituting the given data, we get

$$\log\frac{4.5\times10^7}{1.5\times10^7} = \frac{-E_a}{2.303\times8.314}\left(\frac{1}{373} - \frac{1}{323}\right)$$

which gives $E_a = 22012.7$ J/mol $= 22.13$ kJ/mol.

Problem 12

In the Arrhenius equation for a certain reaction, the value of A and E_a are $4 \times 10^{13}\ s^{-1}$and 98.6 J/K/mol, respectively. If the reaction is of first order, at what temperature will its half period be 10 min?

Solution

We know that

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\times60} = 1.55\times10^{-3}\ \text{s}^{-1}$$

According to Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

Substituting the various values in the above equation, we get

$$\log 1.155 \times 10^{-3} = \log 4 \times 10^{13} - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T}$$

Solving, we get $T = 311.35$ K.

Problem 13

A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ/mol.

Solution

Using Arrhenius equation, we can write

$$k_1 = Ae^{-E_1/RT_1} \quad \text{and} \quad k_2 = Ae^{-E_2/RT_2}$$

Also, from these expressions, it follows that

$$e^{-E_1/RT_1} = e^{-E_2/RT_2} \quad \text{or} \quad \frac{E_1}{RT_1} = \frac{E_2}{RT_2} \quad \text{or} \quad \frac{E_1}{T_1} = \frac{E_2}{T_2}$$

Since, $E_2 = E_1 - 20$ kJ/mol, we get $E_1/T_1 = (E_1 - 20)/T_2$

or

$$E_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{20}{T_2}$$

or

$$E_1 = \frac{20T_1}{T_1 - T_2}$$

Substituting the values of T_1 and T_2, we get

$$E_1 = \frac{(20)(500)}{500 - 400} = 100 \text{ kJ/mol}$$

Problem 14

In the Arrhenius equation for a reaction, the value of frequency factor A = 3.5×10^{10} s^{-1} and energy of activation $E_a = 36.8$ kJ/mol. If the reaction is of first order, at what temperature will its half-life period be 30 min?

Solution

For a first-order reaction,

$$k = \frac{0.693}{t_{1/2}}$$

For half-life period of 30 min = 30 × 60 = 1800 s, the rate constant is

$$k = \frac{0.693}{1800} = 3.85 \times 10^{-4}\ \text{s}^{-1}$$

According to Arrhenius equation,

$$\ln k = \ln A - \frac{E_a}{RT}$$

Given that:

$$A = 3.5 \times 10^{10}\ \text{s}^{-1}$$

$$E_a = 36.8\ \text{kJ/mol} = 36.8 \times 10^3\ \text{J/mol}$$

$$R = 8.314\ \text{J}$$

Substituting the value of k and the above parameters in the equation, we obtain the temperature as

$$\ln 3.85 \times 10^{-4} = \ln 3.5 \times 10^{10} - \frac{36.8 \times 10^3}{8.314 \times T}$$

$$1.348 - 4(2.3026) = 1.253 + 10 \times 2.3026 - \frac{4426.27}{T}$$

$$1.348 - 9.214 = 24.279 - \frac{4426.27}{T}$$

$$-7.8624 - 24.279 = -\frac{4426.27}{T}$$

$$-32.1414 = -\frac{4426.27}{T}$$

Therefore,

$$T = \frac{4426.27}{32.1414} = 137.71\ \text{K} = 14.71^\circ\text{C}$$

Problem 15

The rate of reaction is doubled when the temperature is changed from 298 K to 308 K. Calculate the energy of activation of the reaction.

Solution

The Arrhenius equation can be used to calculate energy of activation, if rate constant at two different temperatures is known

$$E_a = 2.303R\frac{T_1T_2}{T_2 - T_1}\log\left(\frac{k_2}{k_1}\right)$$

Given that $T_1 = 298$ K; $T_2 = 308$ K; $k_2 = 2k_1$; $R = 8.314$ J/K/mol. Substituting these in the equation, we get

$$\begin{aligned}E_a &= 2.303\times 8.314\times\left(\frac{298\times 308}{308-298}\right)\log\left(\frac{2k_1}{1k_1}\right)\\ &= 2.303\times 8.314\times\left(\frac{91784}{10}\right)\log 2\\ &= 2.303\times 8.314\times 9178.4\times 0.301\\ &= 52897.78 \text{ J/mol}\\ &= 52.89 \text{ kJ/mol}\end{aligned}$$

7.6 Theories of Reaction Rates

The theory of reaction rate attempts to account for the observed kinetics of reactions in terms of the molecular behavior of the reacting systems. There are two important theories of reaction rates. These include collision theory developed by Arrhenius and Van't Hoff and the modern transition state theory also known as absolute reaction rate theory or activated complex theory.

Collision Theory

According to this theory, in a bimolecular reaction, two molecules should collide and acquire sufficient energy on collision to bring about the reaction (Figure 6). In fact molecules collide with each other, but all collisions are not sufficiently effective as few acquire activation energy.

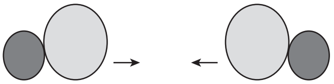
Suppose Z is the number of molecules colliding per cm^3 per second in the reacting system containing 1 mol/l of reactant and q is the fraction of these that are activated, then reaction constant k of the reaction is given by

$$k = Zq \tag{7.38}$$

According to kinetic theory of gases, for a gas containing only one kind of molecule, the number of colliding molecules per cm^3 per second is,

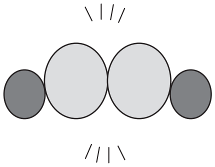
$$Z_1 = \pi\sigma^2 v(n^*)^2 \tag{7.39}$$

where σ is the molecular diameter, v the average molecular velocity in cm/s and n^* the number of molecules per cm^3. On substitution of $v = 0.921\sqrt{(3RT/M)}$ in Eq. (7.39), it becomes



Molecules are approaching each other

(a)



Molecules are colliding

(b)

Molecules move away from each other
without any change – ineffective collision

(c)

Products are formed – effective collision

(d)

Figure 6 Schematic picture indicating nature of collision of molecules.

$$Z_1 = (\sqrt{2}\pi\sigma^2)\left[0.921\sqrt{\frac{3RT}{M}}(n^*)^2\right] = (6.51\times10^4)\sigma^2(n^*)^2\sqrt{\frac{T}{M}} \tag{7.40}$$

When two different molecules are involved, Z is taken to be $Z_{1,2}$ and is given by

$$Z_{1,2} = n_1^* n_2^* \left[\frac{\sigma_1+\sigma_2}{2}\right]^2 \sqrt{8\pi RT\frac{(M_2+M_1)}{M_1M_2}} = 1.14\times10^4(\sigma_1+\sigma_2)n_1^* n_2^* \sqrt{\frac{T(M_2+M_1)}{M_1M_2}} \tag{7.41}$$

where σ_1 and σ_2 are the molecular diameters of the respective molecules, M_1 and M_2 their molecular weights, n_1^* and n_2^* the numbers of the respective molecules per cm^3 at temperature T.

From Maxwell distribution law for molecular rates, it can be deduced that, in any gas containing n^* molecules per cm^3 at a temperature T, the number of these n', which will possess an energy E or higher is

$$n' = n^* e^{-E/RT} \tag{7.42}$$

If $E = E_a$, the energy of activation, the fraction of molecules activated in Eq. (7.42), the fraction of molecules activated can be given as,

$$\frac{n'}{n^*} = e^{E_a/RT} = \frac{\text{Number of molecules activated}}{\text{Total number of molecules}}$$

And this is equal to q. Then, k becomes

$$k = Ze^{E_a/RT} \tag{7.43}$$

Z is given by Eq. (7.40) for same type of molecules and Eq. (7.41) for molecules of different type. The calculation of k theoretically goes along with that experimentally in several gaseous reactions and solution phase reactions. Hence the theory is considered successful. However, there are many reactions of both in gas and solution phases, where the theoretical values are too high by the factors ranging from 10^9 onwards. For such reactions, a probability factor, P is introduced to allow the disparity between calculated and observed rate constants.

$$k = PZe^{-E_a^*/RT} \tag{7.44}$$

where P may have the values ranging from unity to 10^{-9}.

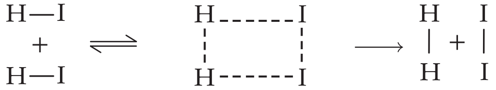
Limitation of Collision Theory

The collision theory is applicable to simple gaseous reactions. The experimental rates of reactions between complicated molecules are found to be much smaller than the theoretically predicted rate. This discrepancy is explained by the fact that the complicated molecules are considered to be hard spheres with no internal energy. The spherical model ignores the dependence of the effectiveness of a collision on the orientation of the molecules colliding. Activation energy includes only translational motion neglecting rotational and vibrational motions. Hence, this theory is applicable to reactions involving simple gas molecules.

Transition State Theory (Absolute Reaction Rate Theory or Activated Complex Theory)

According to this theory, the reactant molecules are not directly converted into products. They are first converted into a highly energized intermediate activated complex or transition state having only a transient existence. The activated complex subsequently breaks up into products. The rate of decomposition of the activated complex determines the rate of reaction. For example,

$$\text{Reactants} \rightleftharpoons \text{Activated complex} \longrightarrow \text{Products}$$



The activation energy of the reaction, according to this theory, is defined as the additional energy which the reactant molecules must acquire to form the intermediate activated complex. From Figure 3, it is clear that there is a small fall in the potential energy of the reactants initially. This may be due to approach of the reactant molecules close to one another before reaching to form the activated complex. Similarly, in the final stage there is a small rise in energy of the products which is due to falling apart of the product molecules after the reaction.

Now since the products possess higher energy than the reactants, the reaction will be endothermic. In such reactions, the activation energy of the reverse reaction will always be less than that of the forward reaction. Activation energy of the reverse reaction means the additional energy which the product molecules must acquire to form the activated complex.

The theory of absolute reaction rates is an alternate approach to reaction kinetics. It is based on statistical mechanics. Here the activated complex is assumed to be stable for some time. A general reaction can be represented by the scheme,

$$\mathrm{A} + \mathrm{B} \rightarrow [\mathrm{AB}]^{*} \rightarrow \text{Products}$$

Eyring showed that the rate constant k for any reaction, is given by

$$k = \left(\frac{RT}{Nh}\right) e^{-\Delta G^{*}/RT} \tag{7.45}$$

In this equation, R is gas constant, N is Avogadro number, h is Planck's constant, T is absolute temperature and ΔG^{*} is free energy of activation. We know that

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*} \tag{7.46}$$

where ΔH^{*} is the heat of activation and ΔS^{*} is the entropy of activation. Inserting Eq. (7.46) into Eq. (7.45), it gives,

$$k = \left(\frac{RT}{Nh}\right) e^{(\Delta H^{*} - T\Delta S^{*})/RT}$$

or

$$k = \left(\frac{RT}{Nh}\right) e^{\Delta H^{*}/RT} \cdot e^{-\Delta S^{*}/R} \tag{7.47}$$

Equation (7.46) is the fundamental relation of this theory for the rate constant of a simple bimolecular reaction. Taking log of both sides of Eq. (7.47) and differentiating with respect to T, it gives

$$\frac{\mathrm{d}(\ln k)}{\mathrm{d}T} = \frac{\Delta H^{*}}{RT^{2}} + \frac{1}{T} = \frac{\Delta H^{*} + RT}{RT^{2}} \tag{7.48}$$

According to Arrhenius equation,

$$\frac{\mathrm{d}(\ln k)}{\mathrm{d}T} = \frac{E_{\mathrm{a}}}{RT^{2}} \tag{7.49}$$

Comparison of Eqs. (7.48) and (7.49) gives,

$$E_{\mathrm{a}} = \Delta H^{*} + RT$$

$$\Delta H^{*} = E_a - RT \tag{7.50}$$

While comparing the above equation with Eq. (7.44), the collision theory shows that essentially

$$PZ = \left(\frac{RT}{Nh}\right) e^{\Delta S^{*}/R} \tag{7.51}$$

And consequently, the difficulty occasioned in the latter theory by the appearance of the probability factor, P can be reconciled by the introduction of the entropy of activation. Although it is not possible to estimate ΔS^{*} for any but the simplest reactions, the theory of absolute reaction rates is satisfactorily successful in elucidating chemical kinetics.

Concept Check

- Explain temperature coefficient of a reaction.
- Write Arrhenius equation and explain the significance of all terms in it.
- What are the important features of collision theory?
- Why is collision theory applicable to simple gaseous molecular reaction?
- Why is the potential energy of the molecules shown lowered in the energy profile diagram of reactants and products?

7.7 Catalysis

A substance that influences the rate of a chemical reaction and remains unchanged during the reaction is called **catalyst**. This phenomenon is known as **catalysis**. For example, the combination of H_2 and O_2 to form water is slow at ordinary temperature. But the reaction proceeds more rapidly in the presence of platinum (Pt). So Pt acts as catalyst in this reaction. Chemical equation of the reaction is given below.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

In some cases the activity of a catalyst is considerably increased by the addition of another substance, which does not have any catalytic property. Such a substance which increases the efficiency of the catalyst is called **promoter**. Molybdenum (Mo) acts as a promoter since it enhances the activity of catalyst (Fe) in the manufacture of NH_3 by Haber's process.

$$N_2 + 3H_2 \underset{Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

In a few cases, a catalyst retards the rate of a reaction. This catalyst is called **negative catalyst** or **inhibitor**. Glycerine or acetanilide acts as inhibitor in the decomposition of H_2O_2.

General Characteristics of Catalysts

Some characteristic features of catalysts are listed as follows:

1. The catalyst remains unchanged in amount and chemical composition at the end of the reaction. However, it may undergo some physical changes.
2. Only a small quantity of the catalyst is generally needed. For example a small quantity of MnO_2 will increase the rate of decomposition of $KClO_3$ appreciably. However, in some homogeneous cat-

alytic reaction, the rate of the reaction is proportional to the concentration of catalyst. For example, the rate of inversion of cane sugar catalyzed by H^+ ions varies with the concentration of H^+ ions. In certain heterogeneous reactions, the rate increases with the increase in area of the catalytic surface. Hence, the efficiency of a solid catalyst increases when it is present in finely divided state.

3. The catalyst does not alter the position of equilibrium in a reversible reaction. It only hastens the approach of equilibrium. This has been verified experimentally.
4. The catalyst does not initiate the reaction. The reaction requires much less energy of activation in presence of a catalyst and hence the reaction takes place faster.
5. The catalyst is generally specific in its action. For example, MnO_2 can catalyze the decomposition of $KClO_3$ but it cannot catalyze the decomposition of $KClO_4$ or KNO_3.
6. A catalyst gets poisoned by certain substances. It has been found that impurities, even if present in small amount, inhibit or retard the rate of catalyzed reactions to a large extent. These impurities are, therefore, called **catalytic poisons**. For example, the rate of combination of SO_2 and O_2 (in Contact process) is slowed down considerably if small amounts of arsenic compounds are present.

Types of Catalysis

The catalysis process may be classified as follows:

1. **Homogeneous catalysis:** In this case, the catalyst is present in the same phase as the reacting substances. For example NO(g) catalyzes the combination of moist SO_2 and O_2 in the lead chamber process for the manufacture of sulphuric acid (H_2SO_4).

$$2SO_2(g) + 2H_2O(g) + O_2(g) \xrightarrow{NO} 2H_2SO_4$$

Mechanism: It is believed that a reactive intermediate compound is first formed by the interaction of one of the reactants with the catalyst. The intermediate compound then reacts with the other reactant or reactants giving the final product and the catalyst is regenerated in its original form simultaneously. For example in lead chamber process,

Step I: The catalyst NO reacts with O_2 which is one of the reactant, to form NO_2 as the intermediate product.

$$\underset{\text{Catalyst}}{2NO} + \underset{\text{Reactant}}{O_2} \rightarrow \underset{\text{Intermediate product}}{2NO_2}$$

Step II: NO_2 so formed combines with the other reactant (SO_2) to form SO_3 as the final product with regeneration of NO.

$$2NO_2 + \underset{\text{Reactant}}{2SO_2} \rightarrow \underset{\substack{\text{Final}\\\text{product}}}{2SO_3} + \underset{\text{Catalyst}}{2NO}$$

SO_3 so obtained combines with H_2O to form H_2SO_4.

2. **Heterogeneous catalysis:** In this catalytic reaction, the catalyst is in a different phase from the reactants. The simplest example of this is the reaction between ethylene and hydrogen in the presence of a nickel catalyst. The reactants are gases whereas the catalyst is a solid. Similarly, solid platinum or V_2O_5 catalyzes the oxidation of SO_2 to SO_3 in Contact process for the manufacture of H_2SO_4.

$$2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3$$

3. **Autocatalysis:** In certain reactions, one of the products acts as the catalyst. The rate of reaction is slow at the beginning of reaction and it increases gradually when product species are formed. One of the product species enhances the rate of reaction. Such product species is called **autocatalyst** and this phenomenon is called **autocatalysis**. For example, the oxidation of oxalic acid by acidified $KMnO_4$ is slow at the beginning of the reaction. It becomes faster as some amount of products are formed. It is because Mn^{2+} formed as one of the products accelerates the rate of reaction. Thus Mn^{2+} is called autocatalyst in this reaction. The chemical reaction taking place is

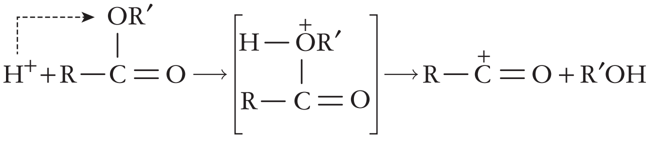
$$2KMnO_4 + 3H_2SO_4 + 5HOOC{-}COOH \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

4. **Induced catalysis:** In this catalytic reaction, one reaction influences the rate of another reaction that does not occur under ordinary conditions. For example, the reduction of $HgCl_2$ by oxalic acid proceeds at a much faster rate in the presence of $KMnO_4$. This is because the reduction of $KMnO_4$ by oxalic acid further induces the reduction of $HgCl_2$.
5. **Acid–base catalysis:** There are some homogeneous catalytic reactions which are brought about by acids or bases. This is known as acid–base catalysis. Hydrolysis of ester in presence of acids is an example of this type of catalysis.

$$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$$

Mechanism: It has been observed that catalytic activity of an acid (or base) for a given reaction depends on its ability to lose (or gain) a proton. Therefore, the mechanism of acid–base catalysis appears to involve loss or gain of protons. It is believed that a complex is formed first by transfer of a proton to the reactant molecule. This process is slow and determines the rate of reaction. By rapid internal rearrangement the product is formed and proton is set free. For example, in the acidic hydrolysis of an ester,

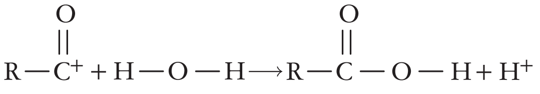
Step I: The proton attacks ester molecule to form a complex, which gives a carbonium ion and a molecule of alcohol.



$$H^+ + R-\overset{\overset{OR'}{|}}{C}=O \longrightarrow \left[\begin{array}{l} H-\overset{+}{O}R' \\ \quad\;\; | \\ R-C=O \end{array}\right] \longrightarrow R-\overset{+}{C}=O + R'OH$$

Complex

Step II: The carbonium ion so formed takes OH^-ions from a molecule of water to form carboxylic acid.



$$R-\overset{\overset{O}{||}}{C^+} + \underset{\text{Water}}{H-O-H} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{||}}{C}-O-H} + H^+$$

6. **Enzyme catalysis:** Enzymes are the proteins with high molecular weight of order 10000 or even more and are derived from living organisms. Each enzyme can catalyze a specific reaction. For example, starch is converted into maltose in presence of diastase, which is an enzyme and is produced in the germinated barley seeds.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}}$$

The enzyme catalyzed reactions are highly sensitive to temperature. Generally, the optimum temperature for maximum enzyme activity varies between 15–25°C. The catalytic activity of enzymes is due to their capacity to lower the activation energy for a particular reaction.

Mechanism: Michaelis and Menten suggested the following mechanism for enzyme-catalyzed reactions.

Let E and S be enzyme and substrate, respectively. Let X be an intermediate complex which is formed when E reacts with S. This is depicted in Eq. (7.52).

$$E + S \xrightarrow{k_1} X \tag{7.52}$$

The intermediate complex so obtained, may either dissociate back into E and S or may give rise to the final product represented as P. These two possibilities are represented by the following equations

$$X \xrightarrow{k_2} E + S \tag{7.53}$$

$$X \xrightarrow{k_3} P \tag{7.54}$$

where k_1, k_2, k_3 are the rate constants for respective reactions. The rate of formation of complex X is given by:

$$\frac{\mathrm{d}[X]}{\mathrm{d}t} = k_1[E][S] - k_2[X] - k_3[X]$$

$$\frac{\mathrm{d}[X]}{\mathrm{d}t} = k_1[E][S] - (k_2 + k_3)[X] \tag{7.55}$$

where $[E]$, $[S]$ and $[X]$ represent molar concentration of the enzyme, substrate and the complex, respectively.

Rate of formation of product as per Eq. (7.54) is given by

$$\frac{\mathrm{d}[P]}{\mathrm{d}t} = k_3[X] \tag{7.56}$$

Equation (7.55) may be written as

$$\frac{\mathrm{d}[X]}{\mathrm{d}t} = k_1\{[E_0] - [X]\}[S] - (k_2 + k_3)[X] \tag{7.57}$$

where $[E_0] = [E] + [X]$.

It may be noted that since $[E]$ represents molar concentration of the unreacted enzyme and $[X]$ represents the concentration of the enzyme which has entered into complex formation, $[E_0]$ stands for total concentration of the enzyme. As the reaction proceeds, the intermediate complex is formed according to Eq.(7.52), and it decomposes instantaneously according to Eqs. (7.53) and (7.54). In other words,

$$\frac{d[X]}{dt} = 0 \tag{7.58}$$

This state is called **stationary state**. At this state, Eq. (7.57) is written as

$$k_1\{[E_0] - [X]\}[S] = (k_2 + k_3)[X]$$

$$k_1[E_0][S] = \{(k_2 + k_3) + k_1[S]\}[X]$$

or

$$[X] = \frac{k_1[E_0][S]}{(k_2 + k_3) + k_1[S]}$$

Substituting the above value of [X] in Eq. (7.56), we get

$$r = \frac{d[P]}{dt} = \frac{k_3k_1[E_0][S]}{(k_2 + k_3) + k_1[S]} \tag{7.59}$$

where r is rate of formation of product.
Dividing numerator and denominator of Eq. (7.59) by k_1,

$$r = \frac{d[P]}{dt} = \frac{k_3[E_0][S]}{(k_2 + k_3)/k_1 + [S]} \tag{7.60}$$

$(k_2 + k_3)/k_1$ is known as **Michaelis constant** and can be denoted as k_m. So, Eq. (7.60) is written as

$$r = \frac{d[P]}{dt} = \frac{k_3[E_0][S]}{k_m + [S]} \tag{7.61}$$

If [S] is very small then Eq. (7.61) can be written as

$$r = \frac{d[P]}{dt} = \frac{k_3[E_0][S]}{k_m}$$

Since k_3, k_m and $[E_0]$ are constants,

$$r \propto [S] \tag{7.62}$$

This means that the reaction will be first order with respect to concentration of substrate.

If $[S] << k_m$, then k_m can be neglected in the denominator giving the maximum rate. Thus the rate of reaction is independent of concentration of substrate. In other words the reaction would be zero order with respect to concentration of substrate.

Industrial Applications of Catalysts

Catalysts are used in different industrial processes. Some commonly used catalysts are given in Table 2.

Table 2 Some Common Catalysts and the processes in which they are used

Name of the Catalyst	*Name of the Process in which the Catalyst is used*
Finely divided iron as catalyst and finely divided Mo as promoter	Manufacture of ammonia by Haber's process
Ziegler–Natta catalyst (Triethylaluminium and titanium tetrachloride)	Preparation of stereospecific polymers
Platinized asbestos or V_2O_5	Manufacture of H_2SO_4 by Contact process

(*Continued*)

Table 2 Continued

Name of the Catalyst	*Name of the Process in which the Catalyst is used*
Cu_2Cl_2	Deacon's process for manufacture of Cl_2
Platinum gauze	Ostwald's process for manufacture of HNO_3
ZnO as catalyst and Cr_2O_3 as promotor	Synthesis of CH_3OH
Fe_2O_3 as catalyst and Cr_2O_3 as promotor	Bosch's process for manufacture of H_2 from water gas and steam
Ni	Hydrogenation of vegetable oil

Concept Check

- Define a catalyst.
- What is a negative catalyst? Give examples.
- Explain heterogeneous catalysis taking a suitable example.
- What is meant by catalytic poisoning? Give examples.
- What is autocatalysis? Explain with examples.
- Write any two enzyme-catalyzed reactions.

Key Terms

Rate of reaction
Rate equation
Order
Molecularity
Integrated rate equation
Half-life period
Activation energy
Threshold energy
Activated complex
Transition state
Arrhenius equation
Catalysis
Heterogeneous catalysis
Homogeneous catalysis
Promotors
Acid–base catalysis
Enzyme catalysis

Objective-Type Questions

Multiple-Choice Questions

1. The unit of zero-order rate constant is
   a. mol/l/s
   b. l/mol/s
   c. s^{-1}
   d. l^2/s
2. Which of the following factors does not influence the rate of reaction?
   a. Temperature
   b. Concentration of reactants
   c. Molecular weight of reactants
   d. Catalyst
3. For a reaction, $aA \rightarrow bB$, the rate of reaction is doubled when the concentration of A is increased by four times. The rate of reaction is equal to
   a. $k[A]^2$
   b. $k[A]^{1/2}$
   c. $k[A]^{3/2}$
   d. $k[A]$
4. For a given reaction, rate $= k[A]^2[B]$ on doubling the concentration of A, the rate of reaction will become

a. two times.
b. three times.
c. four times.
d. remain the same.

5. What is the order of reaction for which rate equation = $k[A]^2 [B]^{1/2}$?
a. 2
b. 5/2
c. 1/2
d. 3/2

6. For oxidation of SO_2 to SO_3, the rate = $k [SO_2] [SO_3]^{-1/2}$, what will be order of reaction when SO_2 is present in excess?
a. −1/2
b. 1/2
c. 1
d. None of the above.

7. Which of the following is not true for molecularity of reaction?
a. It is the number of molecules of reactants taking part in elementary step of a reaction.
b. It is assigned for each elementary step reaction.
c. It provides no information about reaction mechanism.
d. It can have zero, fractional or negative value.

8. Decomposition of N_2O_5 as $2N_2O_5 \rightarrow 4NO_2 + O_2$ is
a. bimolecular and first-order reaction.
b. bimolecular and second-order reaction.
c. bimolecular and zero-order reaction.
d. unimolecular and first-order reaction.

9. The rate constant is given by the equation $k = P \times Ze^{-E_a/RT}$ .Which factor should register a decrease for the reaction to proceed more rapidly?
a. T
b. Z
c. E_a
d. P

10. The rate of a reaction is the same as the rate constant if the order of the reaction is
a. zero.
b. 1.
c. 2.
d. 1.5.

11. The initial concentration of a zero-order reaction is decreased from 4 mol/l to 1 mol/l. For the changed concentration, the half life
a. remains the same.
b. is reduced to one fourth.
c. becomes four times.
d. is doubled.

12. In a second-order reaction, the time needed for the initial concentration of the reactant to reduce of the value is
a. inversely proportional to the initial concentration.
b. independent of the initial concentration.
c. proportional to the initial concentration.
d. proportional to the square of the initial concentration.

13. The reaction: $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ obeys the second-order rate law. When the partial pressure of NO_2 in the reaction mixture is doubled, the rate would
a. remain unchanged.
b. get doubled.
c. become four times the original rate.
d. decrease.

14. A zero-order reaction is the one
a. in which reactants do not react.
b. in which one of the reactants is in large excess.
c. whose rate is not affected by concentration of reactant.
d. whose rate increases with time.

15. The unit of rate constant for a second-order reaction is
a. mol l s.
b. mol/l^2/s.
c. mol/l/s.
d. l/mol/s.

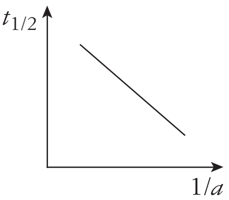
16. For a reaction of second-order kinetics, its $t_{1/2}$ is directly proportional to
   a. a
   b. a^3
   c. a^2
   d. a^{-1}

17. The correct expression for integrated rate law for a first-order reaction is
   a. $k = (2.303/t)\log([A_0]/[A])$
   b. $kt = 2.303\log([A_0]/[A])$
   c. $[A_0] = [A]e^{-kt}$
   d. $\ln([A]/[A_0]) = -kt$

18. The value of rate constant for a first-order reaction for which half life is 5 min is
   a. 0.693 s^{-1}
   b. 2.31×10^{-3} s^{-1}
   c. 0.231 s^{-1}
   d. 23.1 s^{-1}

19. The $t_{1/2}$ for the decomposition of ammonium nitrate (NH_4NO_2) given by $NH_4NO_2 \rightarrow N_2 + H_2O$ is 2 h. The time required for 99.9% of the reaction to complete is
   a. 20 h
   b. 25 h
   c. 15 h
   d. 30 h

20. Which of these is the correct representation for a second-order reaction?

a.


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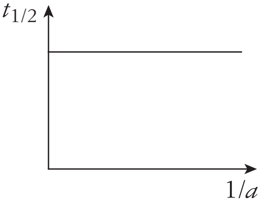

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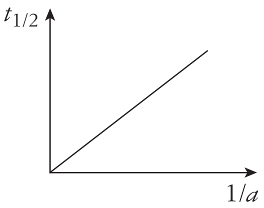
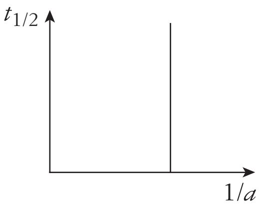


d.


21. In the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate of formation of O_2 is 3.6×10^{-2}mol/l/s. What is the rate of disappearance of N_2O_5?
   a. 3.6×10^{-2}mol/l/s
   b. 1.8×10^{-2}mol/l/s
   c. 7.2×10^{-2}mol/l/s
   d. None of the above.

22. For a first-order reaction $k = 1.5 \times 10^{-3}$ s^{-1}, what is the change in half-life period of the reaction when the initial concentration of the reactants is doubled?
   a. It remains the same.
   b. It becomes double.
   c. It becomes half.
   d. None of the above.

23. The rate of reaction increases with rise in temperature due to
   a. increase in activation energy.
   b. increase in number of effective collisions between molecules.
   c. decrease in threshold energy.
   d. None of the above.

24. The correct expression for Arrhenius equation is
   a. $k = Ae^{E_a/RT}$
   b. $k = Ae^{RT/E_a}$
   c. $k = Ae^{-E_a/RT}$
   d. $k = Ae^{-RT/E_a}$

25. When E_a of a reaction is zero then the rate constant of the reaction is equal to
    a. $2.303k$
    b. $k/2.303$
    c. $t_{1/2}$
    d. A

26. Energy of activation of a reactant is reduced by
    a. increased temperature.
    b. reduced pressure.
    c. increased pressure.
    d. reduced temperature.

27. Activation energy is equal to
    a. threshold energy.
    b. threshold energy + energy of colliding molecules.
    c. threshold energy – energy of colliding molecules.
    d. threshold energy × energy of colliding molecules.

28. In a certain reaction, 10% of the reactant disappeared in 20 min at 37°C and in 5 min at 57°C. The activation energy of the reaction in kJ/mol is
    a. 78.
    b. 65.
    c. 80.
    d. 59.

29. For a certain first-order thermal decomposition of a gaseous substance; the rate constant increases in the ratio 35:3 for an increase in temperature from 45°C to 65°C. What is the approximate magnitude (mean value) of E_a in kcal/mol?
    a. 14.62
    b. 16.42
    c. 26.41
    d. 21.46

30. A catalysis increases the rate of a chemical reaction by
    a. increasing the activation energy.
    b. decreasing the activation energy.
    c. reacting with products.
    d. reacting with reactants.

31. Which one of the following statements is not true?
    a. A catalyst accelerates the rate of the reaction.
    b. In a reversible reaction, the catalyst alters the equilibrium.
    c. A small quantity of catalyst is enough to carry out an appreciable amount of the reaction.
    d. The catalyst remains unchanged chemically in a reaction.

32. The activity of a catalyst is enhanced by the presence of a substance called
    a. super-catalyst.
    b. promoter.
    c. catalytic poison.
    d. none of the above.

33.

Column I	*Column II*
A. Zero-order reaction	1. $-dx/dt = k[A]^2[[B]$
B. First-order reaction	2. $CH_3COOCH_3 + NaOH \rightarrow CH_3COONa + CH_3OH$
C. Second-order reaction	3. $k_{t+10}/k_t \approx 2$ or 3
D. Temperature coefficient	4. dx/dt
E. Instantaneous rate	5. $2H_2O_2 \xrightarrow{h\nu} 2H_2O + O_2$
F. Rate equation for third-order reaction	6. $H_2 + Cl_2 \rightarrow 2HCl$

The correct pairs matching Column I with Column II are:
    a. A-4, B-5, C-2, D-3, E-6, F-1
    b. A-2, B-3, C-4, D-5, E-6, F-1
    c. A-1, B-6, C-2, D-5, E-3, F-4
    d. A-3, B-5, C-6, D-4, E-1, F-2

Fill in the Blanks

1. In the reaction $A + B \rightarrow \text{products}$, if reactant A is taken in excess, then it is an example of ________ reaction.
2. In a first-order reaction, the concentration of a reactant is expressed in moles per liter, the unit of rate constant for the reaction is ________.
3. The number of atoms or molecules taking part in an elementary step leading to the chemical reaction is called ________ of the reaction.
4. The unit for rate constant of a zero-order reaction is ________.
5. The ________ rate law describes the variation of concentration of reactants with time as the reaction proceeds.
6. For a second-order reaction, the half-life period is ________ proportional to the concentration of the reactant.
7. In the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of formation of NH_3 is 4.4×10^{-4}mol/l/s, the rate of consumption of N_2 is ________.
8. For the reaction $2A + B \rightarrow C + D$, the $\text{rate} = k[A]^x[B]^y$, the order of reaction is ________ and the apparent molecularity of reaction is ________.
9. A ________ is a substance which influences the rate of chemical reaction without itself undergoing any permanent chemical change.
10. The half-life period of a reaction is 60 min, on reducing the initial concentration to half, the half-life period is reduced to 30 min, the order of reaction is ________.

Review Questions

Short-Answer Questions

1. What are instantaneous reactions? Give examples.
2. What is meant by rate of reaction?
3. How does concentration of the reactants influence the rate of the reaction?
4. Explain with an example how radiation influences the rate of a reaction.
5. Write the rate equation of the following reaction:

$$nA + mB + pC \rightarrow \text{Products}$$

6. The rate law has the form: $\text{Rate} = k[A][B]^{1/3}$. Can the reaction be an elementary process?
7. Why does the rate of reaction:
   a. increase with increase in temperature?
   b. increase with increase in concentration of reactants?
   c. decrease with the progress of reaction?
8. Define order of a reaction.
9. Predict the order of the following reactions from their rate equations:
   a. $A + B \rightarrow \text{Products}, dx/dt = k[A]^{1/3}[B]^3$
   b. $2A + B \rightarrow \text{Products}, dx/dt = k[A]^2[B]$
10. What are the units of k for first-order and second-order reactions?
11. Define molecularity of a reaction.
12. How does molecularity differ from order of a reaction?
13. A reaction is found to be zero order. Will its molecularity also be zero?

14. Predict the molecularity of the reactions:
    a. $N_2O_4(g) \rightarrow 2NO_2(g)$
    b. $CH_3COOC_2H_5(l) + H_2O(l) \rightarrow CH_3COOH(l) + C_2H_5OH(l)$
15. Can molecularity be fractional or zero? Give reasons for your answer.
16. From the following rate constant values, identify the order of the reaction:
    a. $k = 5.0 \times 10^{-2}$ mol/l/s
    b. $k = 1.2 \times 10^{-3}$ l/mol/s
    c. $k = 7.6 \times 10^{2} s^{-1}$
17. The reaction $2NO_2 + F_2 \rightarrow 2NO_2F$ has been found to be first order with respect to NO_2 and with respect to F_2. Write the rate law equation of the reaction and determine the overall order of reaction.
18. The reaction $2NO + O_2 \rightarrow 2NO_2$ is second order with respect to NO and first order with respect to O_2. The mechanism of the reaction involves two steps

    $$NO + O_2 \rightarrow NO_3 \quad \text{(Slow)}$$

    $$NO + NO_3 \rightarrow 2NO_2 \quad \text{(Fast)}$$

    State the following:
    a. rate law equation.
    b. order of reaction.
    c. molecularity of reaction.
19. Write the integrated rate law equation for zero-order, first-order and second-order reactions and express the units of the rate constants.
20. What is a zero-order reaction? Write the expression for half-life period of this reaction.
21. What is the unit of (a) zero-order reaction and (b) third-order reaction?
22. Why is $t_{1/2}$ of a first-order reaction independent of concentration of reactants?
23. What is the order of a reaction whose $t_{1/2}$ is proportional to $1/a^2$ where a is the initial concentration of the reactant?
24. Define half-life period of a reaction. How does half-life period of a first-order reaction vary with temperature?
25. What is pseudo-unimolecular reaction? Give one example.
26. Explain why the hydrolysis of an ester in the presence of dilute acid follows first-order kinetics while that in the presence of dilute alkali follows the second-order kinetics.
27. How do we know that all collisions between reactant molecules do not lead to a chemical change?
28. Distinguish between activation energy and internal energy of a reaction.
29. Why does the collision theory apply to reactions of simple gaseous molecules?
30. What is meant by Arrhenius factor?
31. Write the mathematical expression for Arrhenius equation.
32. Why is a reaction speeded up in presence of a catalyst?
33. Distinguish between homogeneous and heterogeneous catalysis.
34. What are enzyme reactions? Illustrate with example.
35. Cite an example of a negative catalysis.

Long-Answer Questions

1. What is meant by rate of reaction? Discuss the various factors that affect the rate of reaction.
2. Differentiate between order and molecularity of a reaction. Give two examples showing how they are same and how they are different.

3. Deduce the expression for the rate constant of a first-order reaction and show that the half-life period of a first-order reaction is independent of the initial concentration of the reactant.
4. a. Derive the integrated rate equation for a second-order reaction where the reactants are of same concentration?
   b. Show that the half-life time of such a reaction is inversely proportional to the initial concentration of the reactant.
5. Explain why a second-order reaction behaves as a first-order reaction when one of the reactants is present in large excess.
6. a. What is a zero-order reaction? Derive expression for its rate law.
   b. Show that the half-life time of a zero-order reaction is directly proportional to the initial concentration.
7. What are the characteristic features associated with a first-order reaction?
8. What are the features of a second-order reaction?
9. How would you plot data in order to determine the order of a reaction?
10. Discuss the collision theory of bimolecular reactions.
11. Explain the transition state theory of bimolecular reaction rates.
12. Write down the equation to determine the effect of temperature on rate of reaction. How can this equation be used to determine the activation energy of the reaction?
13. Write an account of the Arrhenius equation for the rate of chemical reactions.
14. a. What is activation energy? Explain its significance with the help of an energy profile diagram.
    b. Explain how a small rise in temperature appreciably increases the rate of reaction.
15. Explain the following terms: (a) activated complex; (b) temperature coefficient of a reaction.
16. a. Explain the transition state theory for reaction rate with the help of energy level diagram.
    b. How does the nature of activated complex change in the presence of a catalyst?
17. What is meant by catalysts? Give the important features of catalytic reactions.
18. Distinguish heterogeneous catalysis from homogeneous catalysis. Explain the theory of heterogeneous catalysis.

Numerical Problems

1. From the following data for the decomposition of ammonium nitrate in aqueous solution, show that the reaction is first order:

Time (min)	10	20	25	∞
Volume of N_2 (ml)	6.25	11.40	13.65	35.05

2. A first-order reaction is 50% complete in 30 min. Calculate the time taken for the reaction to be 75% complete.
3. A substance having a half-life period of 30 min decomposes according to the first-order rate law.
   a. What fraction of this will be decomposed and what will remain behind after 1.5 h?
   b. How long will it take to be 60% decomposed, if its initial concentration is just doubled?
4. A first-order reaction, A → B requires activation energy of 70 kJ/mol. When a 20% solution of A was kept at 25°C for 20 min, 25% decomposition took place. What will be the percentage of decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature.

5. A uranium mineral contains ^{238}U and ^{206}Pb in the ratio 4:1 by weight. Calculate the age of the mineral, given that $t_{1/2}$ for $^{238}U = 4.5 \times 10^9$ years.

6. The pyrolysis of an organic ester follows a first-order process and it can be expressed as

$$\ln k = 78.09 - \frac{42075}{T}$$

where k is given in the units of min^{-1}. Calculate the time required for 25% of reaction to complete at 227°C.

7. The following rate data was obtained in the study of the reaction: A + B → Products.

[A] (mol/1)	0.001	0.005
[B] (mol/l)	0.005	0.010
Initial rate (mol/l/s)	5×10^{-4}	5×10^{-3}

From these data, calculate (a) the order of the reaction with respect to A and B, (b) the total order of the reaction. What is the rate law? Also determine the rate constant of the reaction.

8. The spontaneous decomposition of radioactive nuclei is a first-order rate process. Uranium 238 disintegrates with the emission of α-particle with a half-life of 4.5×10^9 years. If at time $t = 0$, a mol of ^{238}U is present, calculate the number of nuclei left after 1 billion years.

9. A first-order reaction has $k = 1.5 \times 10^{-6}\ s^{-1}$ at 200°C. If the reaction is allowed to run for 10 h, what percentage of the initial concentration would have changed in the product? What is the half life of this reaction?

10. In the hydrolysis of ethyl acetate using mineral acid, the volume of NaOH required for the titration of same volume of reaction mixture after time 0 min, 5 min and ∞ min are 15 ml, 25 ml and 30 ml, respectively. What is the value of rate constant for the reaction?

11. Find the activation energy for the reaction if the ratio of rate constants at two different temperatures 127°C and 27°C is 3.

12. The rate of a first-order reaction is 2×10^{-3}mol/l/s at 0.5 M concentration of the reactant. Find the half life of the reaction in seconds.

13. The rate constant for an isomerization A → B is $4.5 \times 10^{-3}\ min^{-1}$. If initial concentration of A is 1 M, calculate the rate of the reaction after 1 h.

14. In the reduction of nitric oxide gas with hydrogen, the reaction was found to be 50% complete in 224 s when the initial pressure of the mixture was 202 mm Hg. In a second experiment, the time for half the reaction to be completed was 140 s when the initial pressure was 258 mm Hg. Calculate the total order of the reaction.

15. In a reaction, a substance undergoes decomposition which is catalyzed in presence of finely divided nickel. If there are enough sites on the surface of catalyst so that 20 molecules of substance react per second, then what is the rate of reaction for 1.0 M solution?

16. Find out the velocity constant of the decomposition of ammonium nitrite in aqueous solution with the help of the following data:

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Time (min)	10	25	∞
Volume of N_2 (ml)	6.25	13.65	35.05

17. Show by using rate law how much the rate of reaction

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

will change if the volume of reaction vessel is diminished to one-third of its initial volume. The reaction follows first-order kinetics.

18. An experiment requires minimum β-activity produced at the rate of 346 β particles per minute. The half-life period of $^{99}_{42}Mo$, which

is a β-emitter is 66.6 h. Find the minimum amount of $^{99}_{42}\mathrm{Mo}$ required to carry out the experiment in 6.909 h.

19. In a particular reduction process, the concentration of a solution that is initially 0.24 M is reduced to 0.2 M in 10 h and 0.06 M in 20 h. What is the rate constant of this reaction?

20. If three-fourth of a first-order reaction is completed in 32 min, what is the half-life period of the reaction?

21. If half-life of a first-order reaction is 2.31×10^3 min, how long will it take for 1/5 of the reactant to be left behind?

22. Show that for a first-order reaction the time required for 75% completion of reaction is twice the time required for 50% completion of reaction.

23. A substance A is mixed with equal number of moles of another substance B. At the end of 60 s, 30% of reaction is over. How much A and B would be left unreacted at the end of 75 s, if the reaction is first order with respect to both A and B?

24. In a first-order reaction, the concentration of reactants is reduced to one-third the initial concentration in 30 s. Calculate the rate constant. How much time will it take to reduce the initial concentration from 0.5 mol/l to 0.05 mol/l?

25. In a second-order reaction, where the initial concentration of the reactants is the same, half of the reactants are consumed in 30 min. If the rate constant is 3.6×10^{-2} l/mol/min, what is the initial concentration of the reactants?

26. In a second-order reaction, the initial concentration of the reactant is 0.2 mol/l. The reaction was 40% complete in 20 min. Calculate (a) rate constant, (b) time required for 75% completion of reaction and (c) half-life period.

27. A first-order reaction has rate constant equal to $2.5 \times 10^{-3}\ \mathrm{s^{-1}}$ at 273 K and $7.5 \times 10^{-3}\ \mathrm{s^{-1}}$ at 298 K. Calculate the activation energy of the reaction.

28. The specific rate constant for the decomposition of formic acid is $5.5 \times 10^{-5}\ \mathrm{s^{-1}}$ at 413 K. Calculate the rate constant at 458 K, if energy of activation is 2.37×10^4cal/mol.

29. At 380°C, the $t_{1/2}$ for the first-order decomposition of H_2O_2 is 360 min. The energy of activation is 200 kJ/mol. Calculate the time required for 75% decomposition at 450°C.

30. A first-order reaction is 50% completed in 20 min at 27°C, the same reaction is 50% complete in 5 min at 77°C. Calculate the activation energy of the reaction.

31. How many times the rate of reaction increases at 20°C for a reaction having activation energies as 40 kJ/mol and 60 kJ/mol, in the presence and absence of a catalyst, respectively?

32. The rate of reaction becomes three times when the temperature is changed from 298 K to 358 K. Calculate the energy of activation of reaction. Given $R = 8.314$ J/K/mol.

Answers

Multiple-Choice Questions

1. (a)
2. (c)
3. (b)
4. (c)
5. (b)
6. (a)
7. (c)
8. (a)
9. (c)

10. (a)
11. (b)
12. (a)
13. (c)
14. (c)
15. (d)
16. (d)
17. (b)
18. (b)
19. (a)
20. (c)
21. (c)
22. (a)
23. (b)
24. (c)
25. (d)
26. (a)
27. (b)
28. (d)
29. (c)
30. (b)
31. (b)
32. (b)
33. (a)

Fill in the Blanks

1. pseudo-unimolecular
2. s^{-1}
3. molecularity
4. mol/l/time
5. integrated
6. inversely
7. 2.2×10^{-4}/mol/l/s
8. $x + y$; 3
9. catalyst
10. zero

Numerical Problems

2. 60.2 min
3. (a) 0.126; (b) 39.7 min
4. $x = 67.17\%$
5. 14.4×10^{8} years
6. 123 min
7. (a) 1, 0 (b) 1, Rate law = k[A], $k = 0.5\ s^{-1}$
8. 5.13×10^{23} years
9. 128.33 h
10. 0.22 min^{-1}
11. 11 kJ
12. 173.25 s
13. 3.43×10^{-23} M/min
14. 3
15. 3.32×10^{3} M/s
16. 0.0197 min^{-1}
17. Rate becomes 27 times faster
18. 4.77×10^{-16} mol/l
19. $6.9 \times 10^{-2}\ h^{-1}$
20. 16 min
21. 536.599 min
23. 65%
24. 0.0366 s^{-1}; 62.9 s
25. 0.926 mol/l
26. (a) 0.1667 mol/l/min; (b) 90 min; (c) 30 min.
27. 29.73 kJ/mol
28. $9.397 \times 10^{-4}\ s^{-1}$
29. 20.8 min
30. 24.205 kJ/mol
31. 7516.23 times.
32. 16.242 kJ/mol

8

Electrochemistry

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Origin and nature of electrode potential.
- Electrochemical cells and their types.
- Electrochemical conventions and cell representation.
- Different types of reference electrodes and their applications.
- Characteristics and applications of electrochemical series.
- Derivation and significance of Nernst equation.
- Electromotive force (EMF) of a cell and its measurement.
- Determination of pH of a solution.
- Essential components and characteristics of a battery.
- Characteristics and uses of fuel cells and their types.
- Corrosion, its definition, causes and effects.
- Types of corrosion – dry and wet (electrochemical) corrosion – and their differences.
- Types of electrochemical corrosion – differential metal, differential aeration (including waterline, pitting and crevice).
- Other types of corrosion – stress, intergranular, microbiological, soil, erosion.

Electrochemistry is the branch of chemistry that deals with the relationship between chemical changes taking place in chemical reactions and electrical energy. It deals with the study of electrical properties of solutions of electrolytes and also the chemical changes brought about by electrical energy. Thus, it enables us to elucidate how chemical energy produced in a redox reaction can be converted into electrical energy and how electrical energy can be used to bring about a redox reaction which is otherwise non-spontaneous.

8.1 Electrode Potential

Origin of Electrode Potential

An electrode is a metal plate or rod dipped in a solution of its own ions. A galvanic cell is made up of two such electrodes and current flows from one electrode to the other. This indicates that the two electrodes of the cell are at different potentials. Also, redox reactions occur in a galvanic cell. It is necessary to draw a relation between all these observations to help us to know how potential arises in an electrode.

In order to understand the origin of potential of an electrode, consider a zinc electrode which consists of a Zn strip dipped in $ZnSO_4$ of any concentration. Nernst proposed that in the electrode, there will appear two tendencies – oxidation and reduction processes. If the tendency, say oxidation occurs in the electrode, the Zn atoms on the surface of the metal undergo oxidation, leaving behind electrons on the surface.

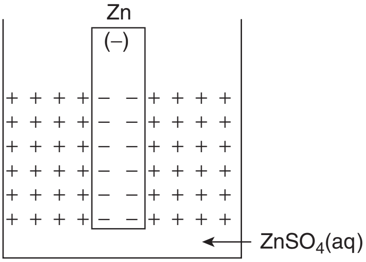


Figure 1 Origin of electrode potential (oxidation).

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e^-$$

The Zn^{2+} ions pass into the solution, hence the metal strip becomes negatively charged. The positively charged metal ions in the solution would accumulate around the metal in an order (Figure 1). If the other tendency – reduction occurs in this electrode, then Zn^{2+} ion in the solution would undergo reduction by grabbing electrons from the metallic surface (Figure 2).

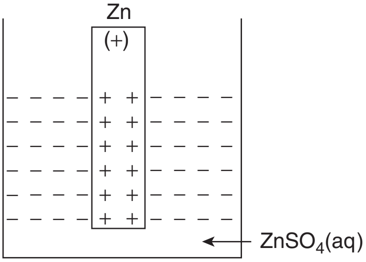


Figure 2 Origin of electrode potential (reduction).

$$\mathrm{Zn}^{2+} + 2e^- \rightarrow \mathrm{Zn}$$

With this, the metallic surface becomes positively charged. The negatively charged ions in the solution would accumulate around the metal. The two tendencies happen simultaneously on the same electrode. As the two tendencies oppose each other, it can be visualized that equilibrium exists between them:

$$\mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{2+} + 2e^-$$

Hence, an electrical double layer called **Helmholtz electrical double layer** (HED) is established at the metal–aqueous solution interface. The actual tendency of the electrode (to gain or lose electrons) depends on which direction the equilibrium would shift to. If the equilibrium shifts in the forward direction, oxidation occurs. If the equilibrium shifts in the backward direction, reduction occurs.

Across the HED layer, there is movement of charges. This results in the build up of potential called **electrode potential**. It is defined as the potential that exists between the metal or a gas and its ions in aqueous solution, at their equilibrium when they are in contact with each other. The electrode potential of a metal is thus a measure of its tendency to lose or gain electrons when in contact with a solution of its own salt.

Oxidation Potential

If oxidation occurs at the electrode, the potential of the electrode can be termed as oxidation potential. For the zinc electrode, the reaction can be represented as:

$$\mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{2+} + 2e^-$$

The electrode in which oxidation occurs at equilibrium is referred to as a negative electrode. For example, the oxidation potential of zinc electrode with 1 M $ZnSO_4$ at 298 K is +0.76 V.

Reduction Potential

If reduction occurs at the electrode, the potential of the electrode is referred to as reduction potential. For the zinc electrode, the reaction can be represented as:

$$\mathrm{Zn}^{2+} + 2e^- \rightleftharpoons \mathrm{Zn}$$

If reduction occurs at equilibrium in an electrode, it is termed as positive electrode. The reduction potential of a zinc electrode with 1 M $ZnSO_4$ at 298 K is −0.76 V.

By comparing the oxidation and reduction potential values of the same electrode, the spontaneous reaction occurring in the electrode can be predicted. In case of zinc electrode, the oxidation potential is more positive than its reduction potential. Thus, oxidation is a spontaneous reaction. However, polarity of an electrode depends on the other electrode to which it is connected.

Standard Electrode Potential (E°)

It is defined as the potential that exists between the metal or the gas and its aqueous solution of unit concentration at 298 K when the sum of all partial pressures of the gaseous reactants and products, if any, is equal to 1 atm pressure. This value is considered to compare the relative abilities of different electrodes to undergo oxidation or reduction reaction.

Concept Check

- Explain the origin of electrode potential.
- The standard reduction potential of zinc is −0.76 V. Explain.
- Two electrodes A and B have potentials of −0.28 V and −0.44 V, respectively. Identify the oxidation and reduction electrodes, if they are coupled.

8.2 Cells

The devices which convert electrical energy into chemical energy or vice versa are called **cells**. Based on the activity taking place in them, these devices are classified into two major categories:

1. Electrolytic cells.
2. Electrochemical cells or galvanic cells (voltaic cells):

The devices in which physical or chemical changes occur in the presence of applied electrical energy are referred to as **electrolytic cells**. The devices in which electrical energy is generated on account of the chemical reactions occurring in them are known as **galvanic cells**. Common example of galvanic cell is Daniell cell in which the following cell reaction takes place:

$$\mathrm{Zn} + \mathrm{CuSO_4} \rightarrow \mathrm{ZnSO_4} + \mathrm{Cu}$$

Galvanic cells may be classified into chemical and concentration cells. Further, chemical cells are classified into two categories, namely primary and secondary cells.

Redox Reactions

In any reaction, a substance can lose electrons to be oxidized, only if there is another present, which will readily accept these electrons and get reduced. Such reactions in which oxidation and reduction take place simultaneously are known as redox reactions. For example, in the reaction:

$$\mathrm{Zn + CuSO_4 \rightarrow ZnSO_4 + Cu}$$

Zn loses two electrons and gets oxidized, whereas copper gains two electrons and is reduced from Cu^{2+} to Cu. Redox reactions may be termed as direct or indirect redox reactions depending on whether both oxidation and reduction are taking place in the same or different vessels, respectively. In most of electrochemical cells, indirect redox reactions take place and can be expressed in terms of half-cell reactions. The overall reaction is represented in terms of two reactions, one representing the oxidation and the other representing the reduction. For instance, in the earlier example, the half reaction may be written as:

Overall redox reaction: $\mathrm{Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)}$

Oxidation half reaction: $\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2}e^-$

Reduction half reaction: $\mathrm{Cu^{2+}(aq) + 2}e^- \mathrm{\rightarrow Cu(s)}$

Concept Check

- Differentiate between electrolytic and galvanic cells.
- Using the cell reaction,

  $$\mathrm{3X + 4Y^{3+} \rightleftharpoons 3X^{4+} + 4Y}$$

  Write down the half-cell reactions.

8.3 Galvanic Cells

A galvanic cell consists of two electrodes immersed in solutions of their respective salts. When the two electrodes are connected externally, a redox reaction occurs in which one of the electrodes undergoes oxidation while the other undergoes reduction.

Construction and Working

A galvanic cell consists of anode compartment and a cathode compartment connected by a salt bridge. Oxidation occurs at anode (negative electrode) while reduction occurs at the cathode (positive electrode). Daniell cell is the most popular galvanic cell. It has two electrodes: Zn in $ZnSO_4$ and Cu in $CuSO_4$ connected by a salt bridge (Figure 3).

When the electrodes are externally connected, oxidation occurs at zinc electrode as shown below.

$$\mathrm{Zn \rightleftharpoons Zn^{2+} + 2}e^-$$

Zinc atoms lose two electrons each and come into the solution in the form of Zn^{2+} ions. The electrons liberated from zinc electrode move along external connection to the copper electrode and this results in generation of electricity. Copper ions accept these electrons and are converted to copper. At the copper electrode, reduction reaction occurs, as shown below.

$$\mathrm{Cu^{2+} + 2}e^- \rightleftharpoons \mathrm{Cu}$$

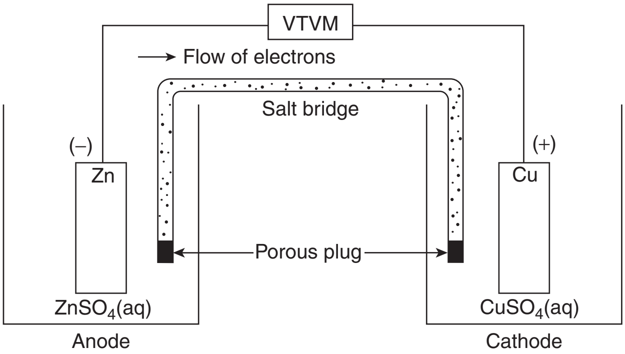


Figure 3 Galvanic cell.

The net reaction taking place in the cell is

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Zn}^{2+} + \mathrm{Cu}$$

Hence, a redox reaction takes place in a galvanic cell. Electrodes are named in accordance with the reaction occurring at them. In a Daniell cell, zinc electrode is called **oxidation electrode** or **anode** and copper electrode is called **reduction electrode** or **cathode**.

Salt Bridge

If the electrodes in a galvanic cell are not connected internally, initially the cell generates electrical energy. The electrodes get polarized with passage of time and the cell stops working. For continuous generation of electrical energy, the electrodes need to be internally connected.

A salt bridge is usually used to connect two compartments of a galvanic cell. It consists of a gel taken in a clean U-tube. The gel is formed by adding agar–agar into boiling water containing a suitable electrolyte like KCl. Generally, KCl is preferred because the ionic conductances of K^+ and Cl^- are almost the same. The gel holds the electrolyte in the tube as shown in Figure 4.

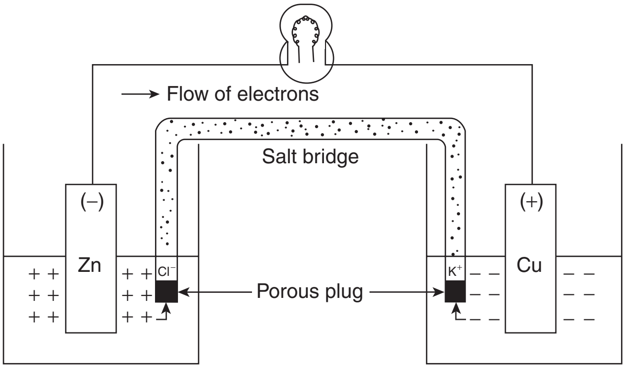


Figure 4 Salt bridge and electrolyte.

As the reactions proceed in the galvanic cell, there will be accumulation of particular ions around the electrodes. For example, Zn electrode is surrounded by positively charged ions as it acquires negative charge and Cu electrode is surrounded by negatively charged ions. This results in a slow down of the electrode reactions. From the electrolyte of the salt bridge, say KCl, the K^+ and Cl^- ions migrate towards the ends of the salt bridge; K^+ ions would migrate towards the reduction electrode (cathode) while Cl^- ions would migrate towards the oxidation electrode (anode). At the oxidation electrode (anode), Cl^- ions would polarize (attract) some of the positively charged ions towards themselves. Simultaneously, K^+ ions would move towards the reduction electrode (cathode) and polarize the negatively charged ions surrounding the metal. Thus, the cell works as usual.

Hence, a salt bridge helps to

1. bring about internal contact between the electrodes;
2. minimize liquid junction potential;
3. minimize polarization.

Concept Check

- Describe the working and construction of a Daniell cell.
- What are the reactions taking place at cathode and anode in a galvanic cell with zinc and copper electrodes?
- A salt bridge reduces polarization of a Zn–Ni cell. Explain.

8.4 Electrochemical Conventions and Cell Representations

There are some universal conventions and notations which are adopted in describing and representing an electrode or a galvanic cell. These are given as follows:

1. A galvanic cell consists of two compartments which are connected with each other by a salt bridge.
2. Each compartment contains a solution of an electrolyte and an electrode. It is also called a half-cell.
3. Oxidation reaction takes place in one half-cell whereas reduction reaction takes place in the other half-cell.
4. The half-cell in which oxidation takes place is called the **oxidation half-cell** and the electrode present in it is called oxidation electrode or anode. This electrode is also called **negative electrode**.
5. Similarly, that half-cell in which reduction reaction takes place is called **reduction half-cell**. The electrode in it is called reduction electrode or cathode. It is also called **positive electrode**.
6. The potential of an electrode is called **oxidation potential** if oxidation reaction occurs at this electrode. Similarly, the potential of the electrode is called **reduction potential**, if reduction reaction takes place at this electrode. Oxidation potential of an electrode posseses the same magnitude with opposite sign as the reduction potential of that electrode. For example, standard oxidation potential of Zn is +0.76 V, while standard reduction potential of it is −0.76 V. However, according to IUPAC conventions, the potential of an electrode is always expressed in terms of reduction potential irrespective of the reaction occurring at the electrode.
7. A cell can be represented by writing the components of oxidation half-cell at the left hand side and that of reduction potential at the right hand side. These two are separated by means of a double vertical line (i.e., $||$), which represents the salt bridge. The symbol of the electrode and the formula of electrolyte are separated by comma (,) or a single vertical line ($|$). While representing the cell,

concentration of the electrolyte is also written within brackets after its formula. For example, the Daniell cell can be represented as:

$$\mathrm{Zn}|\mathrm{ZnSO_4}(1\ \mathrm{M})||\mathrm{CuSO_4}(1\ \mathrm{M})|\mathrm{Cu}$$

8. The EMF of a cell is represented as:

$$E_{\mathrm{cell}} = E_{\mathrm{R}} - E_{\mathrm{L}} = E_{\mathrm{cathode}} - E_{\mathrm{anode}}$$

whereE_{R} and E_{L} are the reduction potentials of RHS and LHS electrodes, respectively.

Concept Check

- Construct a galvanic cell using the following electrodes. Given that E^o (Au$^+$, Au) = + 1.69 V and E^o (Hg^{2+}, Hg) = + 0.86 V.
- The standard oxidation potential of Cd ($E^o_{\mathrm{Cd^{2+}/Cd}}$) and standard reduction potential of Ag ($E^o_{\mathrm{Ag^{+}/Ag}}$) is 0.40 V and 0.80 V, respectively. What is the EMF of the cell?

8.5 Reference Electrodes

The potential of an electrode cannot be accurately and directly measured. It is not feasible to connect a measuring device to the solution of electrode, as it may lead to another equilibrium along with the existing one. The problem can be overcome if the electrode is connected to another electrode of known potential. Such an electrode is termed as **reference electrode**. From the measured EMF, the potential of the electrode can be obtained by subtracting the potential of the reference electrode.

Any electrode of known potential cannot be treated as a reference electrode. The criteria for an electrode to act as a reference electrode are:

1. The potential of such an electrode should be known, under the conditions of utility.
2. The potential of the electrode should show minimum variation with temperature. In other words, the potential gradient with respect to temperature should be minimum.

The most commonly used reference electrode is the **standard hydrogen electrode** (SHE). The potential of all other electrodes are measured with respect to the hydrogen electrode. Hence, it is called a **primary reference electrode**.

There are a few more reference electrodes available which are standardized by using standard hydrogen electrode (SHE) and then used as reference electrodes for measuring potential of other electrodes. Such reference electrodes are termed as **subsidiary** or **secondary reference electrodes**. Calomel electrode and silver–silver chloride electrode are the most popular secondary reference electrodes.

Standard Hydrogen Electrode (Normal Hydrogen Electrode)

A standard (normal) hydrogen electrode (SHE/NHE) consists of a platinum foil dipped in 1.0 M HCl solution. The platinum foil is enclosed in a thick-walled glass tube and connected to an external contact wire. Pure hydrogen is passed into the container at 1 atm pressure through the inlet at the top. Excess of hydrogen leaves the electrode through the outlet at the bottom (Figure 5). Pure hydrogen gets adsorbed onto the Pt surface and is in contact with H$^+$ ions in the solution. It forms a reversible electrode for which standard electrode potential (E^o) is conventionally considered as zero.

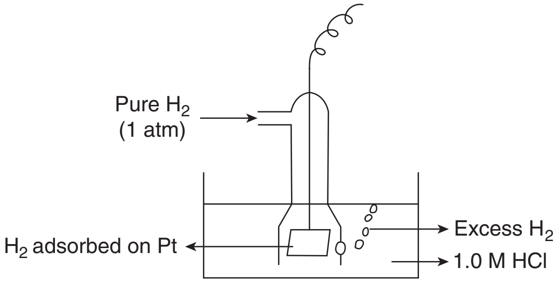


Figure 5 Standard hydrogen electrode.

SHE acts as a half cell in a galvanic cell, when it is connected to another half-cell through salt bridge. If it acts as oxidation half-cell, oxidation reaction occurs as follows:

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

This half-cell can be represented as: Pt, H_2(g) (1 atm)|HCl (1.0 M)
When it acts as reduction half-cell, reduction reaction takes place at this electrode as follows:

$$2H^+ + 2e^- \rightleftharpoons H_2$$

This half-cell can be represented as: HCl (1.0 M)|H_2(g) (1 atm), Pt
However, SHE/NHE has its own inherent limitations:

1. It is difficult to maintain unit molar concentration of hydrogen throughout and to pass hydrogen always at exactly 1 atm pressure.
2. Presence of arsenic compounds would easily get adsorbed on platinum foil, thereby poisoning the surface. It would affect the equilibrium of the reaction.
3. In addition, SHE cannot be used in presence of strong oxidizing and reducing agents.

Calomel Electrode

Calomel electrode is a **secondary reference electrode** and belongs to the category of metal–sparingly soluble salt electrodes. Calomel is the common name for mercurous chloride and it is sparingly soluble in water. The electrode consists of a thin layer of pure mercury at the bottom of a gas tube having a side tube at each side as shown in Figure 6. It is covered with a paste of Hg_2Cl_2. A solution of known concentration of KCl (decinormal, normal or saturated) is introduced above the paste. A platinum wire sealed into a glass tube is introduced to make electrical contact with the outer circuit.

This electrode may act as anode or cathode in a galvanic cell. When it acts as an anode, oxidation reaction occurs. Hg undergoes oxidation to form Hg_2^{2+} ions, which combine with Cl^- ions furnished by KCl to form sparingly soluble Hg_2Cl_2. The half-cell reaction may be represented as:

$$2Hg(l) \rightleftharpoons Hg_2^{2+} + 2e^-$$

$$Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_2(s)$$

$$2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e^-$$

This half-cell can be represented as: Hg|Hg_2Cl_2(s)||KCl

When it acts as a cathode reduction reaction occurs. Hg_2^{2+} ions furnished by sparingly soluble Hg_2Cl_2 take up electrons to form Hg. Hence, more and more calomel would pass into the solution. The reaction may be represented as:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+} + 2Cl^-$$

$$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$$

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$$

The cell may be represented as: $\|KCl|Hg_2Cl_2(s)|Hg$

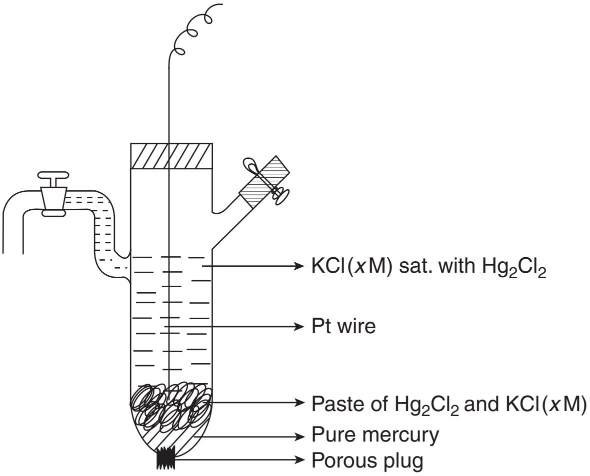


Figure 6 Calomel electrode.

The potential of the calomel electrode is measured by connecting it with standard hydrogen electrode (SHE). It depends on the concentration of KCl solution. The reduction potentials of calomel electrode for 0.1 N and 0.1 N KCl solutions are 0.335 V and 0.2810 V, respectively.

Concept Check

- Calomel electrode is a reference electrode. Justify.
- Presence of impurities in the hydrogen gas poisons the SHE. Justify the statement.

8.6 Electrochemical Series

Standard electrode potentials of various electrodes can be measured by using standard hydrogen electrode (SHE). By convention, standard reduction potentials of various electrodes are tabulated in the increasing order of their standard reduction potential values, indicating their tendency towards reduction or to behave as cathode with respect to SHE. The resulting series is called **electrochemical** or **electromotive** or **activity series** of elements. The electrode with greater reduction potential (E^o) behave as cathode with respect to other electrode having smaller reduction potential.

A typical electrochemical series is given in Table 1.

Table 1 Electrochemical series

Electrode Systems	*Reduction Half Reaction*	*Standard Reduction Electrode Potential E^o (Volts)*
Li^+/Li	$Li^+ + e^- \rightleftharpoons Li$	− 3.024
K^+/K	$K^+ + e^- \rightleftharpoons K$	− 2.924
Ca^{2+}/Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	− 2.87
Na^+/Na	$Na^+ + e^- \rightleftharpoons Na$	− 2.714
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	− 2.36
Al^{3+}/Al	$Al^{3+} + 3e^- \rightleftharpoons Al$	− 1.7
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	− 0.76
Cr^{3+}/Cr	$Cr^{3+} + 2e^- \rightleftharpoons Cr$	− 0.74
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	− 0.441
Cd^{2+}/Cd	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	− 0.402
Ni^{2+}/Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	− 0.236
Sn^{2+}/Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	− 0.14
Pb^{2+}/Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	− 0.126
Fe^{3+}/Fe	$Fe^{3+} + 3e^- \rightleftharpoons Fe$	− 0.045
$H^+/\frac{1}{2}H_2$	$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$	− 0.000
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+ 0.34
Ag^+/Ag	$Ag^+ + e^- \rightleftharpoons Ag$	+ 0.79
Hg^{2+}/Hg	$Hg^{2+} + 2e^- \rightleftharpoons Hg$	+ 0.851
Pt^{2+}/Pt	$Pt^{2+} + 2e^- \rightleftharpoons Pt$	+ 1.2
Au^{3+}/Au	$Au^{3+} + 3e^- \rightleftharpoons Au$	+ 1.38
F^-/F_2	$\frac{1}{2}F + e^- \rightleftharpoons F^-$	+ 2.87

The *characteristics* of electrochemical series are as follows:

1. Lithium is the first member of the series.
2. Highly reactive metal systems are at the top of the series.

3. In other words, good reducing agents are at the top of the series.
4. All good oxidizing agents are at the bottom of the series.
5. Hydrogen system is at the middle of the series. All the elements which displace hydrogen from dilute acids are placed above it.
6. If the standard oxidation potential of an element is lower than that of the other, then the former element acts as a stronger reducting agent as compared to latter. For example, the standard reduction potential of Zn ($E^o_{Zn^{2+}/Zn}$) is less than that of Cu ($E^o_{Cu^{2+}/Cu}$); hence Zn is a stronger reducing agent than copper. In other words, *lower the standard reduction potential, stronger is the reducing ability*.
7. A metal placed higher in the series is anodic to other metals which lie below it. An element can displace all elements that lie below it in the series, from their salt solutions. For example, zinc shavings added to a hot saturated solution of $CuSO_4$ can displace copper from the salt. In other words, displacement reactions can be predicted.
8. Knowledge of electrochemical series helps in selection of electrode assemblies, to construct the galvanic cells of the desired EMF.
9. Spontaneity and feasibility of the cell under construction can be easily predicted.

Applications of Electrochemical Series

1. **Calculation of standard EMF of a cell:** An electrochemical cell is constructed by connecting two half-cells, each of which contains one electrode. Standard electrode potential of these electrodes are known from electrochemical series. Standard EMF of the cell can calculated by putting these values in the following formula.

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

2. **Prediction of spontaneity of the cell reaction:** A reaction is said to be spontaneous if standard change in free energy (ΔG^o) is negative. We know that $\Delta G^o = -nFE^o$, where n is the number of electrons involved, F is the quantity of electricity and E^o is the EMF of the cell at standard conditions.

   Standard change in free energy (ΔG^o) is negative if EMF of the cell at standard conditions (E^o) is positive. The value of E^o can be obtained from the values of standard electrode potential of respective electrodes, which is obtained from electrochemical series. Thus, spontaneity or feasibility of a cell reaction can be predicted with the help of electrochemical series.

3. **Determination of equilibrium constant of a reaction:** We know that standard change in free energy (ΔG^o) = $- RT\ln K$, where K is the equilibrium constant.
   Again we have known that $\Delta G^o = -nFE^o$, where E^o is the EMF of the cell at standard conditions.
   Comparing the above two expressions, we get

$$- RT\ln K = -nFE^o$$

or

$$2.303\ RT \log K = nFE^o$$

or

$$\log K = \frac{nFE^o}{2.303RT} \qquad (8.1)$$

   where n is the number of electrons transferred during the cell reaction which can be known from the equation, F is the quantity of electricity obtained during the cell reaction, R is universal gas constant, which is known, T is the temperature at which the cell reaction is carried out and E^o is the standard EMF of the cell which can be calculated from the values of standard electrode potential of respective electrodes. Standard electrode potentials are obtained from electrochemical series. Thus, the value of equilibrium constant can be determined with the help of electrochemical series.

4. **Prediction of reactions of metals with dilute acids to liberate hydrogen gas:** An element having lower standard reduction potential ($E^{\text{o}}_{\text{red}}$) can reduce (or donate electron) to the other element having higher standard reduction potential. So elements having lower $E^{\text{o}}_{\text{red}}$ than that of hydrogen can reduce it from its solution. In such case H^+ ions present in acids are reduced and hydrogen gas is liberated. Thus, elements such as Al, Zn, Fe, etc. lying above hydrogen in electrochemical series possess low $E^{\text{o}}_{\text{red}}$ value than that of hydrogen and can liberate hydrogen gas from dilute acids.

Problem 1

Calculate the equilibrium constant for the following cell: $\text{Mg}|\text{Mg}^{2+}(\text{aq})\,||\,\text{Ag}^{+}(\text{aq})\,|\,\text{Ag}$. *Given that* $E^{\text{o}}_{Mg^{2+}/Mg} = -2.37$ *V and* $E^{\text{o}}_{Ag^{+}/Ag} = 0.80$ *V.*

Solution

We know that $E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{cathode}} - E^{\text{o}}_{\text{anode}}$
In the given cell, Mg acts as anode and Ag acts as cathode.

So, $$E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{Ag}^{+}/\text{Ag}} - E^{\text{o}}_{\text{Mg}^{2+}/\text{Mg}}$$

or $$E^{\text{o}}_{\text{cell}} = 0.80 - (-2.37) = 3.17 \text{ V}$$

Number of electrons transferred in the cell reaction (n) = 2.

Again we know that $\log K = \dfrac{nFE^{\text{o}}}{2.303RT}$

or $$\log K = \frac{nE^{\text{o}}}{0.0591} = \frac{2 \times 3.17}{0.0591}$$

or $$K = 1.89 \times 10^{107}$$

Problem 2

The electrode potentials of two half reactions are as follows:

$$\text{Fe}^{3+} + e^{-} \rightarrow \text{Fe}^{2+} \qquad E^{\text{o}} = 0.76 \text{ V}$$

$$\text{Ce}^{4+} + e^{-} \rightarrow \text{Ce}^{3+} \qquad E^{\text{o}} = 1.60 \text{ V}$$

Can Ce^{3+} *be oxidized by* Fe^{3+}*? Give reason.*

Solution

Oxidation of Ce^{3+} by Fe^{3+} can be represented by the following reaction:

$$\text{Ce}^{3+} + \text{Fe}^{3+} \rightarrow \text{Ce}^{4+} + \text{Fe}^{2+}$$

Two half reactions are:

$$\text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + e^{-} \text{ (oxidation)}$$

$$\text{Fe}^{3+} + e^{-} \rightarrow \text{Fe}^{2+} \text{ (reduction)}$$

Standard EMF of the cell is given by

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = E^{o}_{Fe^{3+}/Fe} - E^{o}_{Ce^{4+}/Ce}$$

or
$$E^{o}_{cell} = 0.76 - 1.60 = -0.84 \text{ V}$$

Since E^{o}_{cell} is negative, ΔG^{o} is positive. Hence, Ce^{3+}cannot be oxidized by Fe^{3+}.

Concept Check

- What do you understand by electrochemical series? How does it help in predicting the feasibility of a redox reaction?
- Why does copper get deposited on iron nails when immersed in a solution of copper sulphate? Will it happen with platinum pieces? Give reason.

8.7 Nernst Equation

The potential of an electrode depends on concentration and temperature. Therefore, a quantitative equation relating the electrode potential with these parameters can be tailored. Walter Herman Nernst has deduced such an equation for the electrode potential. If the electrolyte concentration is different from 1M and temperature is different from 298 K, the electrode potential can be obtained by using Nernst equation.

Derivation

The derivation of expression for Nernst equation involves the following steps:

1. Consider an electrode assembly undergoing a spontaneous reaction.

$$M^{n+} + ne^{-} \rightleftharpoons M$$

2. If this system is in equilibrium, then as per law of mass action, the equilibrium constant (*K*) can be evaluated as

$$K = \frac{[M]}{[M^{n+}]}$$

3. As the reaction proceeds, there is the formation of HED. Across the HED, there is movement of charges. Hence, some amount of electrical work is done. This value becomes maximum at equilibrium and is referred to as W_{max}.
4. W_{max} depends on
   - the number of coulombs of charges flowing across the interface and
   - the energy available per coulombs of charge.

   The expression for W_{max} can be written as

$$W_{max} = (\text{Number of coulombs of charge flowing across the HED}) \times (\text{Energy available per coulombs of charge})$$

   Therefore,

$$W_{max} = (nF)(E)$$

or
$$W_{\text{max}} = nEF \tag{8.2}$$

Note:

- As per Faraday's second law, 1 mole of electrons ≡ 1 Faraday of charge. So, n mol ≡ nF of charge.
- As per definition, energy available per coulomb is called the potential, measured in volts.

5. As the reaction is spontaneous, there is decrease in the free energy. Also, the decrease in free energy appears as work done (W_{max}). Mathematically,

$$-\Delta G = W_{\text{max}} = nEF$$

where negative sign indicates that ΔG is decreasing. So,

$$-\Delta G = nEF \tag{8.3}$$

Similarly,

$$-\Delta G^{\text{o}} = nE^{\text{o}}F \tag{8.4}$$

where ΔG^{o} and E^{o} are the change in free energy and electrode potential under standard conditions, respectively.

6. ΔG varies with temperature, at equilibrium of the system. Van't Hoff's equations bring about their relation:

$$\Delta G = \Delta G^{\text{o}} + RT \ln \frac{a_{\text{products}}}{a_{\text{reactants}}} \tag{8.5}$$

where T is the temperature on Kelvin scale, a_{products} is activity of products, $a_{\text{reactants}}$ is activity of reactants and R is universal gas constant.

7. Substituting Eqs. (8.3) and (8.4) in Eq. (8.5) gives:

$$-nEF = -nE^{\text{o}}F + 2.303\, RT \log \frac{a_{\text{products}}}{a_{\text{reactants}}}$$

Dividing by nF throughout, we get

$$E = E^{\text{o}} - \frac{2.303\, RT}{nF} \log \frac{a_{\text{products}}}{a_{\text{reactants}}} \tag{8.6}$$

where n is the number of electrons involved and F is quantity of electricity, that is, 96,500 C.
In dilute solutions, activities may be replaced by molar concentrations. Therefore,

$$E = E^{\text{o}} - \frac{2.303RT}{nF} \log \frac{[\text{M}]}{[\text{M}^{n+}]} \tag{8.7}$$

For pure solids, [M] = 1. Therefore, Eq. (8.6) can be written as

$$E = E^{\text{o}} - \frac{2.303}{nF} RT \log \frac{1}{[\text{M}^{n+}]} \tag{8.8}$$

Equation (8.8) is known as **Nernst equation for an electrode** where E is the electrode potential of the electrode (M), E^{o} is the standard electrode potential of electrode and $[\text{M}^{n+}]$ is the concentration of metal ions in solution.

Let M_1 be a metal which is in contact with M_1^{n+} ions in solution constituting a half-cell. The half-cell reaction may be written as $\text{M}_1^{n+} + ne^- \rightleftharpoons \text{M}_1$. According to Nernst equation, the reduction potential of the electrode can be written as

$$E_{\mathrm{M}_1^{n+}/\mathrm{M}_1} = E^{\mathrm{o}}_{\mathrm{M}_1^{n+}/\mathrm{M}_1} - \frac{RT}{nF}\ln\frac{[\mathrm{M}_1]}{[\mathrm{M}_1^{n+}]} \tag{8.9}$$

Putting the values of R, F and T (298 K), we get

$$E_{\mathrm{M}_1^{n+}/\mathrm{M}_1} = E^{\mathrm{o}}_{\mathrm{M}_1^{n+}/\mathrm{M}_1} - \frac{2.303\times 8.303\times 298}{n\times 96500}\log\frac{1}{[\mathrm{M}_1^{n+}]}$$

or

$$E_{\mathrm{M}_1^{n+}/\mathrm{M}_1} = E^{\mathrm{o}}_{\mathrm{M}_1^{n+}/\mathrm{M}_1} - \frac{0.0591}{n}\log\frac{1}{[\mathrm{M}_1^{n+}]} \tag{8.10}$$

Let M_2 be a metal which is in contact with M_2^{n+} ions in solution constituting a half-cell. The half-cell reaction may be written as $\mathrm{M}_2^{n+} + ne^- \rightleftharpoons \mathrm{M}_2$. Applying Nernst equation, we get

$$E_{\mathrm{M}_2^{n+}/\mathrm{M}_2} = E^{\mathrm{o}}_{\mathrm{M}_2^{n+}/\mathrm{M}_2} - \frac{0.0591}{n}\log\frac{1}{[\mathrm{M}_2^{n+}]} \tag{8.11}$$

If the first half-cell acts as anode and the second as cathode, the cell potential or EMF of the cell is given as

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} = E_{\mathrm{M}_2^{n+}/\mathrm{M}_2} - E_{\mathrm{M}_1^{n+}/\mathrm{M}_1} \\ &= \left\{E^{\mathrm{o}}_{\mathrm{M}_2^{n+}/\mathrm{M}_2} - \frac{0.0591}{n}\log\frac{1}{[\mathrm{M}_2^{n+}]}\right\} - \left\{E^{\mathrm{o}}_{\mathrm{M}_1^{n+}/\mathrm{M}_1} - \frac{0.0591}{n}\log\frac{1}{[\mathrm{M}_1^{n+}]}\right\} \\ &= \left\{E^{\mathrm{o}}_{\mathrm{M}_2^{n+}/\mathrm{M}_2} - E^{\mathrm{o}}_{\mathrm{M}_1^{n+}/\mathrm{M}_1}\right\} - \frac{0.0591}{n}\left\{\log\frac{1}{[\mathrm{M}_2^{n+}]} - \log\frac{1}{[\mathrm{M}_1^{n+}]}\right\} \end{aligned}$$

or

$$E_{\text{cell}} = E^{\mathrm{o}}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\mathrm{M}_1^{n+}]}{[\mathrm{M}_2^{n+}]} \tag{8.12}$$

Equation (8.12) is known as **Nernst equation for a galvanic cell**.
The reactions taking place in the cell can be represented as

At the anode: $\mathrm{M}_1 \rightleftharpoons \mathrm{M}_1^{n+} + ne^-$

At the anode: $\mathrm{M}_2^{n+} + ne^- \rightleftharpoons \mathrm{M}_2$

The overall cell reaction: $\mathrm{M}_1 + \mathrm{M}_2^{n+} \rightleftharpoons \mathrm{M}_1^{n+} + \mathrm{M}_2$

So,

$$E_{\text{cell}} = E^{\mathrm{o}}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]} \tag{8.13}$$

In general, for a galvanic cell the EMF is given as:

$$E_{\text{cell}} = E^{\mathrm{o}}_{\text{cell}} - \frac{2.303RT}{nF}\log K \tag{8.14}$$

where K is the equilibrium constant for the reaction.

The Nernst equation is a useful tool in electrochemistry and has the following applications:

1. The potential of an electrode and EMF of a cell can be calculated at any temperature and concentration.

2. Knowing potential of an electrode, the concentration of the reactant can be calculated.
3. The concentration of a solution in the galvanic cell can be determined.
4. The pH of a solution can be calculated by measuring the EMF.

Problem 3

Calculate the electrode potential of copper, if the concentration of $CuSO_4$ *is 0.206 M at 23.1°C. Given that* $E^{o}_{Cu^{2+}/Cu} = +0.34\ \mathrm{V}$.

Solution

Given that

$$[\mathrm{CuSO_4}] = 0.206;\ T = 296.1\ \mathrm{K}$$

The reaction taking place is

$$\mathrm{Cu}^{2+} + 2e^- \rightleftharpoons \mathrm{Cu};\quad n = 2$$

According to Nernst's equation,

$$E_{Cu^{2+}/Cu} = E^{o}_{Cu^{2+}/Cu} - \frac{2.303RT}{nF}\log\frac{1}{[\mathrm{Cu}^{2+}]}$$

or

$$E_{Cu^{2+}/Cu} = +0.34 - \frac{2.303\times 8.314\times 296.1}{2\times 96500}\times\log\frac{1}{0.206} = 0.31984\ \mathrm{V}$$

Problem 4

Calculate the EMF of the following Zn–Ag cell at 22.3°C if the concentration of $ZnSO_4$ *and* $AgNO_3$ *are 0.191 M and 0.0289 M, respectively. Given that* $E^{o}_{Zn^{2+}/Zn} = -0.76\,\mathrm{V}$ and $E^{o}_{Ag^{+}/Ag} = +0.8\,\mathrm{V}$

Solution

From the given values, we have $E^{o}_{Zn^{2+}/Zn} < E^{o}_{Ag^{2+}/Ag}$.

Hence, zinc electrode is an oxidation electrode, whereas silver electrode is a reduction electrode. The cell representation is

$$\mathrm{Zn}|\mathrm{ZnSO_4}(0.191\,\mathrm{M})\,||\,\mathrm{Ag}^+(0.0289\,\mathrm{M})\,|\,\mathrm{Ag}$$

The reaction occurring in the cell is

Oxidation electrode: $\mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{2+} + 2e^-$

Reduction electrode: $(\mathrm{Ag}^+ + e^- \rightleftharpoons \mathrm{Ag})\times 2$

The overall cell reaction: $\mathrm{Zn} + 2\mathrm{Ag}^+ \rightleftharpoons \mathrm{Zn}^{2+} + \mathrm{Ag}$

Therefore,

$$Q = \frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Ag}^+]^2}$$

where Q represents the quotient of reactant and products. According to Nernst equation,

$$\begin{aligned}
E_{\text{cell}} &= E^{\text{o}}_{\text{cell}} - \frac{2.303RT}{nF}\log Q \\
&= \left[E^{\text{o}}_{\text{Ag}^+/\text{Ag}} - E^{\text{o}}_{\text{Zn}^{2+}/\text{Zn}}\right] - \frac{2.303RT}{nF}\ \log Q \\
&= [+0.8 - (-0.76)] - \frac{2.303 \times 8.314 \times 295.3}{2 \times 96{,}500}\ \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \\
&= +1.56 - \frac{2.303 \times 8.314 \times 295.3}{2 \times 96500}\ \log \frac{0.191}{(0.0289)^2} \\
&= 1.4908\ \text{V}
\end{aligned}$$

Problem 5

Calculate the concentration of $NiCl_2$ in the nickel electrode having a potential of – 0.16942 V at 24.9°C. Given that $E^{\text{o}}_{\text{Ni}^{2+}/\text{Ni}} = -0.14\,\text{V}$.

Solution

Applying the Nernst equation,

$$E_{\text{Ni}^{2+}/\text{Ni}} = E^{\text{o}}_{\text{Ni}^{2+}/\text{Ni}} - \frac{2.303RT}{nF}\ \log \frac{1}{[\text{Ni}^{2+}]}$$

Here $n = 2$. So,

$$-0.16942 = -0.14 + \frac{2.303 \times 8.314 \times 297.9}{2 \times 96500}\ \log(x)$$

where $x = [\text{Ni}^{2+}]$. So,

$$\begin{aligned}
-0.16942 &= -0.14 + (0.02955)\ \log x \\
-0.02942 &= 0.02955\ \log x
\end{aligned}$$

Solving, we get $x = [\text{NiCl}_2] = 0.1010$ M.

Problem 6

Calculate the standard electrode potential of lead electrode, if the electrode potential is −0.18025 V at 301 K and a concentration of Pb^{2+} solution is 0.0096 M.

Solution

Given $[\text{Pb}^{2+}] = 0.0096$ M; $E_{\text{Pb}^{2+}/\text{Pb}} = -0.18025$ V; $T = 301$K. According to Nernst's equation,

$$E_{\text{Pb}^{2+}/\text{Pb}} = E^{\text{o}}_{\text{Pb}^{2+}/\text{Pb}} - \frac{2.303RT}{nF}\ \log \frac{1}{[\text{Pb}^{2+}]}$$

Therefore,

$$\begin{aligned}E^{\mathrm{o}}_{\mathrm{Pb^{2+}/Pb}} &= E_{\mathrm{Pb^{2+}/Pb}} - \frac{2.303RT}{nF}\log[\mathrm{Pb}^{2+}]\\ &= -0.18025 - \frac{2.303\times 8.314\times 301}{2\times 96500}\log(0.0096)\\ &= -0.18025 - 0.02986\times(-2.0177) = 0.1200\ \mathrm{V}\end{aligned}$$

Problem 7

For the cell $\mathrm{Zn}|\mathrm{Zn}^{2+}(a=10^{-4})||\mathrm{Mg}^{2+}(a=10^{-3})|\mathrm{Mg}$ *, the standard reduction potential for Zn and Mg electrodes are –0.764* V *and –2.364* V*, respectively.*
(a) Write the half-cell reaction and the overall cell reaction.
(b) Find E^{o}_{cell} *and* ΔG *and predict if the cell reaction is spontaneous or not.*

Solution

For the cell $\mathrm{Zn}|\mathrm{Zn}^{2+}(a=10^{-4})||\mathrm{Mg}^{2+}(a=10^{-3})|\mathrm{Mg}$

(a) Half-cell reactions are:

At the anode: $\mathrm{Zn(s)} \rightarrow \mathrm{Zn}^{2+} + 2e^{-}$

At the cathode: $\mathrm{Mg}^{2+} + 2e^{-} \rightarrow \mathrm{Mg(s)}$

The overall cell reaction: $\mathrm{Zn} + \mathrm{Mg}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Mg}$

(b) According to Nernst equation:

$$E_{\mathrm{cell}} = E^{\mathrm{o}}_{\mathrm{cell}} - \frac{0.0591}{n}\log\frac{[\mathrm{Zn}^{2+}][\mathrm{Mg}]}{[\mathrm{Zn}][\mathrm{Mg}^{2+}]}$$

Substituting given values:

$$\begin{aligned}E_{\mathrm{cell}} &= (E^{\mathrm{o}}_{\mathrm{Mg^{2}/Mg}} - E^{\mathrm{o}}_{\mathrm{Zn^{2+}/Zn}}) - \frac{0.0591}{2}\log\frac{[10^{-4}]}{[10^{-3}]}\\ &= -2.364-(-0.764) - \frac{0.0591}{2}\log 10^{-1}\\ &= 1.6 + \frac{0.0591}{2} = -1.6 + 0.0295 = -1.5705\end{aligned}$$

Therefore,

$$\begin{aligned}\Delta G &= -nFE_{\mathrm{cell}} = -2\times 96500\times -1.5705\\ &= 303106.5\ \mathrm{J/mol} = 303.106\ \mathrm{kJ/mol}\end{aligned}$$

Since E_{cell} is negative and ΔG is positive, the reaction is not spontaneous and feasible.

Problem 8

Calculate the potential of copper–silver cell if $\{Ag^+\} = 1 \times 10^{-3}$ *M and* $\{Cu^{2+}\} = 1 \times 10^{-4}$ *M. The standard reduction potentials of silver and copper electrodes are 0.8 V and 0.3 V, respectively. The cell reaction is given by:*

$$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

Solution

Given that $[Ag^+] = 10^{-3}$ M, $[Cu^{2+}] = 10^{-4}$ M and $n = 2$. Also, $E^o_{Ag^+/Ag} = 0.8\,V$ and $E^o_{Cu^{2+}/Cu} = 0.3\,V$. According to Nernst equation:

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Ag][Cu^{2+}]}{[Ag^+][Cu]}$$

Substituting given values, we get

$$\begin{aligned} E_{cell} &= E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{[10^{-4}]}{[10^{-3}]} \\ &= (0.8 - 0.3) - \frac{0.0591}{2}\log 10^{-1} \\ &= 0.5 - 0.0295 = 0.5295\ V \end{aligned}$$

Problem 9

Calculate the EMF of the cell

$$Pb(s)|Pb^{2+}(1\,M)||Cu^{2+}(1\,M)|Cu(s)$$

Given that

$$Pb(s)\,|\,Pb^{2+}(1M)\,||\,Zn^{2+}(1M)\,|\,Zn(s)\ E^o_{cell} = -0.63\ V$$

$$Cu(s)|Cu^{2+}(1\,M)||Zn^{2+}(1\,M)|Zn(s) \quad E^o_{cell} = -0.010\ V$$

Solution

We know that

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

For $Pb(s)|Pb^{2+}(1M)||Cu^{2+}(1M)|Cu(s)$

$$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{Pb^{2+}/Pb} \tag{8.15}$$

For $Pb(s)\,|\,Pb^{2+}(1M)\,||\,Zn^{2+}(1M)\,|\,Zn(s)$

$$E^o_{cell} = E^o_{Zn^{2+}/Zn} - E^o_{Pb^{2+}/Pb} = -0.63 \tag{8.16}$$

For $\mathrm{Cu(s)|Cu^{2+}(1\,M)||Zn^{2+}(1\,M)|Zn(s)}$

$$E^{\mathrm{o}}_{\mathrm{cell}} = E^{\mathrm{o}}_{\mathrm{Zn^{2+}/Zn}} - E^{\mathrm{o}}_{\mathrm{Cu^{2+}/Cu}} = -1.010 \tag{8.17}$$

Subtracting Eq. (8.17) from Eq. (8.16), we get

$$E^{\mathrm{o}}_{\mathrm{Zn^{2+}/Zn}} - E^{\mathrm{o}}_{\mathrm{Pb^{2+}/Pb}} - (E^{\mathrm{o}}_{\mathrm{Zn^{2+}/Zn}} - E^{\mathrm{o}}_{\mathrm{Cu^{2+}/Cu}}) = -0.63 - (-1.010)$$

or

$$E^{\mathrm{o}}_{\mathrm{Cu^{2+}/Cu}} - E^{\mathrm{o}}_{\mathrm{Pb^{2+}/Pb}} = 0.47\ \mathrm{V}$$

Problem 10

What will be the EMF of a cell at 298 K constructed by dipping zinc rods in 0.001 M and 0.5 M $ZnSO_4$ solutions?

Solution

For a concentration cell at 298 K,

$$E_{\mathrm{cell}} = \frac{0.0591}{n}\log\left[\frac{c_2}{c_1}\right]$$

Substituting given values, we get

$$\begin{aligned} E_{\mathrm{cell}} &= \frac{0.0591}{2}\log\frac{0.5}{0.001} \\ &= 0.0295\log 500 \\ &= 0.0295 + 2.698 = 0.079\ \mathrm{V} \end{aligned}$$

Problem 11

Calculate the maximum work that can be obtained from the cell

$$\mathrm{Zn|Zn^{2+}(1\,M)||Ag^{+}(1\,M)|Ag}$$

where $E^{\mathrm{o}}_{\mathrm{Zn^{2+}/Zn}} = -0.76$ V and $E^{\mathrm{o}}_{\mathrm{Ag^{+}/Ag}} = 0.8$ V.

Solution

The EMF of the cell can be obtained from Nernst equation for the cell reaction

$$\mathrm{Zn + 2Ag^{+} \rightarrow Zn^{2+} + 2Ag}$$

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Zn}^{2+}][\text{Ag}]^2}{[\text{Ag}^+]^2[\text{Zn}]}$$

$$= 0.8 - (-0.76) - \frac{0.0591}{2}\log\frac{[1]}{[1]^2}$$

$$= 1.56 - \frac{0.0591}{2}\times 0 = 1.56\text{ V}$$

As, $\Delta G = -W_{\max} = -nFE$. Therefore,

$$W_{\max} = 2\times 96500\times 1.56 = 301080\text{ J} = 301.080\text{ kJ}$$

Concept Check

- Write the expression for Nernst equation and give the significance of the terms.
- In a particular system, M^{3+} is reduced to M^{2+}. Write down the expression for the potential of the electrode system.

8.8 Applications of EMF Measurement

Determination of Solubility Product and Solubility of Sparingly Soluble Salt

Let us consider a sparingly soluble salt AgCl, whose solubility product and solubility is to be determined. For this a cell may be constructed as follows: Ag electrode is placed in 0.01 M $AgNO_3$. This may be considered as cathode. Another half-cell is constituted by placing Ag electrode into 0.01 M KCl. The two half-cells are connected by a salt bridge. A drop of $AgNO_3$ is added to KCl solution. Small amount of AgCl so formed is sufficient to give its saturated solution. The cell is represented by:

$$\text{Ag}|\text{AgCl}, \text{KCl (0.01 M)} \,||\, \text{AgNO}_3\text{(0.01 M)}\,|\,\text{Ag}$$

Let the concentration of Ag^+ in the solution be c moles/liter at the anode. The cell so constructed is a concentration cell with respect to Ag^+ ions. A silver electrode is in contact with a solution of Ag^+ of known concentration (0.01M) while the other silver electrode is in contact with a solution of unknown concentration of Ag^+. So, EMF of the cell at 25°C can be given as:

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - 0.0591\log\frac{c}{0.01}$$

$$E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{cathode}} - E^{\text{o}}_{\text{anode}} = E^{\text{o}}_{\text{Ag}^+/\text{Ag}} - E^{\text{o}}_{\text{Ag}^+/\text{Ag}} = 0$$

$$E_{\text{cell}} = 0.0591\log\frac{0.01}{c} \tag{8.18}$$

E_{cell} is measured potentiometrically. Concentration of Ag^+ in solution (c) is determined by putting the value of E_{cell} in Eq. (8.18).

It is assumed that KCl is completely dissociated. So the concentration of Cl^- is 0.01 M. Solubility product of AgCl can be given by:

$$K_{sp} = [Ag^+][Cl^-] = (c)(0.01)$$

or

$$K_{sp} = 0.01c \tag{8.19}$$

Let the solubility of AgCl be S mol/l.

$$\underset{}{AgCl} \rightarrow \underset{S}{[Ag^+]} + \underset{S}{[Cl^-]}$$

So,

$$K_{sp} = [Ag^+][Cl^-] = S^2$$

$$S = \sqrt{K_{sp}} \tag{8.20}$$

Putting the value of K_{sp} in Eq. (8.20), solubility of AgCl can be determined. Thus solubility of a sparingly soluble salt can be determined by EMF measurement.

Determination of pH of a Solution

The various electrodes used for determination of pH are described as follows.

Standard Hydrogen Electrode

Standard hydrogen electrode (SHE) may be employed to determine the pH of an unknown solution. It is required to construct a half-cell in order to calculate the pH. The half-cell is constructed by dipping Pt electrode in a solution whose pH is to be determined, taken in a container. A slow current of H_2 gas at 1 atm is bubbled through the solution. The electrode so formed in the half-cell is called hydrogen electrode. The half-cell reaction may be represented by the following equation.

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g)$$

Nernst equation involving the half-cell reaction at 25°C can be written as:

$$E_{H^+/H_2} = E^o_{H^+/H_2} - \frac{2.303RT}{nF}\log\frac{[H_2]^{1/2}}{[H^+]} \tag{8.21}$$

where E_{H^+/H_2} is the electrode potential of the hydrogen electrode present in the half-cell and $E^o_{H^+/H_2}$ is the electrode potential of standard hydrogen electrode, which is taken as zero. Also, R is universal constant = 8.314 J/K/mol, T is temperature in Kelvin scale, n is the number of electrons involved in the reaction and F is the quantity of electricity (96500 C). Substituting these values in Eq. (8.21), we get

$$E_{H^+/H_2} = 0 - 0.0591\log\frac{1}{[H]^+}$$

$$E_{H^+/H_2} = -0.0591[-\log(H^+)]$$

$$E_{H^+/H_2} = -0.0591\text{pH} \tag{8.22}$$

The above half-cell so formed is connected to SHE through a salt bridge. As a result a cell is formed. It can be represented as:

$$\text{Pt}, H_2(g)(1\text{atm}) \mid H^+(\text{unknown conc.}) \parallel H^+(1\text{M}) \mid H_2(g)(1\text{atm}), \text{Pt}$$

The EMF of the cell is given by:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} = E_{\text{R}} - E_{\text{L}} \\ &= E^{\text{o}}_{\text{H}^+/\text{H}_2} - E_{\text{H}^+/\text{H}_2} \\ &= 0 - (-0.0591\text{pH}) \end{aligned}$$

or

$$\text{pH} = \frac{E_{\text{cell}}}{0.0591} \tag{8.23}$$

E_{cell} can be measured with the help of a potentiometer. Putting the value of E_{cell} in Eq. (8.23), pH of the given solution can be determined.

Saturated Calomel Electrode

Let us consider a solution whose pH is to be determined by EMF measurement. This solution is taken in a container and Pt electrode is inserted into it. A slow current of H_2 gas at 1 atmosphere is bubbled through the solution. As a result, a half-cell is constructed. The electrode present in this half-cell is called hydrogen electrode. The half-cell reaction is represented as follows.

$$\text{H}^+(\text{aq}) + e^- \rightleftharpoons \tfrac{1}{2}\text{H}_2(\text{g})$$

Nernst equation involving this half-cell reaction at 25°C can be written as:

$$E_{\text{H}^+/\text{H}_2} = E^{\text{o}}_{\text{H}^+/\text{H}_2} - \frac{2.303RT}{nF}\log\frac{[\text{H}_2]^{1/2}}{[\text{H}^+]}$$

where $E_{\text{H}^+/\text{H}_2}$ is the electrode potential of the hydrogen electrode present in the half-cell and $E^{\text{o}}_{\text{H}^+/\text{H}_2}$ is the electrode potential of standard hydrogen electrode, which is taken as zero.

$$E_{\text{H}^+/\text{H}_2} = 0 - 0.0591\log\frac{1}{[\text{H}]^+}$$

$$E_{\text{H}^+/\text{H}_2} = -0.0591\text{pH}$$

Thus, pH of the solution is determined if the value of $E_{\text{H}^+/\text{H}_2}$ is known. In order to determine $E_{\text{H}^+/\text{H}_2}$, the half-cell is connected to a saturated calomel electrode. As a result a galvanic cell is constructed. The cell can be represented as:

$$\text{Pt}, \text{H}_2(1\,\text{atm})\,|\,\text{H}^+(\text{unknown conc.})\,||\,\text{KCl(saturated)}, \text{Hg}_2\text{Cl}_2(\text{s})\,|\,\text{Hg}$$

Since standard electrode potential of saturated calomel electrode (0.2422 V) is greater than that of hydrogen electrode ($E^{\text{o}}_{\text{H}^+/\text{H}_2} = 0$), saturated calomel electrode acts as cathode in this cell.
The EMF of the cell is calculated from the following relation:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{R}} - E_{\text{L}} \\ &= 0.2422 - E_{\text{H}^+/\text{H}_2} \\ &= 0.2422 - (-0.0591\text{pH}) \\ &= 0.2422 + 0.0591\text{pH} \end{aligned}$$

or

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.0591} \tag{8.24}$$

E_{cell} can be determined potentiometrically. Putting the value of E_{cell} in Eq. (8.24), pH of the given solution is determined.

Quinhydrone Electrode

The pH of a solution can be determined using quinhydrone electrode. Quinhydrone is an equimolar mixture of quinone ($C_6H_4O_2$) and hydroquinone ($C_6H_6O_2$). The electrode is set up by adding a pinch of it into a solution in which Pt electrode is inserted. The pH of this solution is to be determined. The reaction for the half-cell is given as:

$$\underset{(\text{Q})}{C_6H_4O_2} + 2H^+ + 2e^- \rightleftharpoons \underset{(\text{QH}_2)}{C_6H_6O_2}$$

Nernst equation involving this half-cell reactionat 25°C can be written as:

$$E_{(\text{H}^+,\text{Q},\text{QH}_2)} = E^{\text{o}}_{(\text{H}^+,\text{Q},\text{QH}_2)} - \frac{0.0591}{2}\log\frac{[\text{QH}_2]}{[\text{Q}][\text{H}^+]^2} \tag{8.25}$$

$$E_{(\text{H}^+,\text{Q},\text{QH}_2)} = E^{\text{o}}_{(\text{H}^+,\text{Q},\text{QH}_2)} - \frac{0.0591}{2}\log\frac{[\text{QH}_2]}{[\text{Q}]} - \frac{0.0591}{2}\log\frac{1}{[\text{H}^+]^2} \tag{8.26}$$

$$E_{(\text{H}^+,\text{Q},\text{QH}_2)} = E^{\text{o}}_{(\text{H}^+,\text{Q},\text{QH}_2)} - \frac{0.0591}{2}\log\frac{[\text{QH}_2]}{[\text{Q}]} - \frac{2(0.0591)}{2}(-\log[\text{H}^+]) \tag{8.27}$$

Since hydroquinone (QH_2) is a weak acid, it ionizes to a small extent in an acidic solution or in a solution for which pH less than 7. This implies that the concentration of hydroquinone (QH_2) and quinone (Q) present in quinhydrone electrode, remains constant in an acidic solution. Their concentration is same in quinhydrone as it is an equimolar mixture of both. Let the solution for which pH is to be determined be acidic in nature. Therefore, the concentration of hydroquinone (QH_2) is equal to that of quinone (Q) in that solution and hence $[QH_2]/[Q] = 1$.

Equation (8.27) can be written as:

$$E_{(\text{H}^+,\text{Q},\text{QH}_2)} = E^{\text{o}}_{(\text{H}^+,\text{Q},\text{QH}_2)} - 0.0591\text{pH} \tag{8.28}$$

The standard reduction potential of quinhydrone electrode is 0.6996 V.

So, Eq. (8.28) becomes

$$E_{(\text{H}^+,\text{Q},\text{QH}_2)} = 0.6996 - 0.0591\ \text{pH} \tag{8.29}$$

The potential of quinhydrone electrode is determined by connecting it with a saturated calomel electrode. The cell may be represented as:

$$\text{Hg}\,|\,\text{Hg}_2\text{Cl}_2(\text{s}), \text{KCl(sat.)}\,||\,\text{H}^+(\text{unknown conc.})\text{Q}\,|\,\text{QH}_2, \text{Pt}$$

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = E_{(\text{H}^+,\text{Q},\text{QH}_2)} - 0.2422 = 0.6996 - 0.0591\ \text{pH} - 0.2422$$

or

$$E_{\text{cell}} = 0.4554 - 0.0591\ \text{pH}$$

or
$$\text{pH} = \frac{0.0455 - E_{\text{cell}}}{0.0591} \tag{8.30}$$

E_{cell} is calculated potentiometrically. Putting the value of E_{cell} in Eq. (8.30), pH of the solution can be determined.

The **advantages** of quinhydrone electrode are as follows:

1. It can be set up easily as compared to hydrogen electrode.
2. The electrode gives accurate results even in the presence of oxidizing ions, which usually interfere with the working of hydrogen electrode.

The **disadvantages** of quinhydrone electrode are as follows:

Quinhydrone electrode cannot be used in a solution of pH more than 8. It is because hydroquinone being an acid, ionizes appreciably in strongly alkaline solution and also gets oxidized partly by atmospheric oxygen. This alters the equilibrium between quinone and hydroquinone, which forms the basis of the cell reaction.

Glass Electrode

Glass electrode is made up of a special glass of relatively low melting point and high electrical conductivity. It consists of a glass bulb in which 0.1M HCl is taken. A platinum wire is inserted into it to make electrical contact. It is shown in Figure 7.

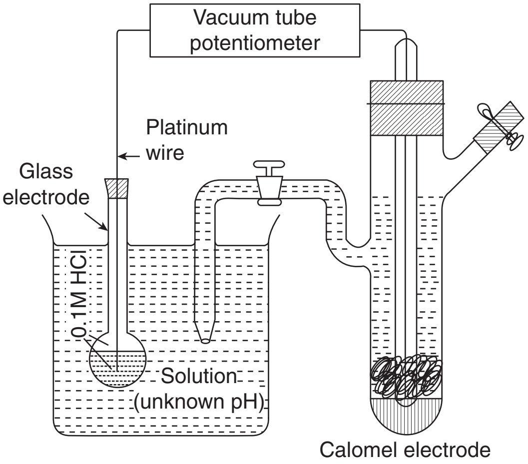


Figure 7 Determination of pH of a solution by glass electrode.

Glass electrode is inserted into a solution in order to determine its pH. It has been observed that a difference in potential exists at the interface between glass and solution containing H^+ ions. The magnitude of this difference in potential depends on quality of glass and concentration of H^+ ions. As a result, a half-cell is constructed. The electrode potential of this half-cell at 25°C can be given by Nernst equation:

$$E_G = E_G^o + 0.0591 \log[H^+]$$

$$E_G = E_G^o - 0.0591 \text{ pH} \tag{8.31}$$

where E_G^o is a constant for the given glass electrode. The electrode reaction is assumed to involve the reduction of H^+ ions. The glass electrode functions as a reversible hydrogen electrode. Glass electrode so constructed is coupled with a saturated calomel electrode in order to construct a cell. The cell may be represented as:

$$\text{Pt, HCl (0.1M), glass}|\text{Soln. of unknown pH}||\text{ KCl (sat.), }Hg_2Cl_2(s)|\text{ Hg}$$

The EMF of such cell is calculated as follows:

$$E_{\text{cell}} = E_{\text{calomel}} - E_G = 0.2422 -(E_G^o - 0.0591 \text{ pH})$$

or

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422 + E_G^o}{0.0591} \tag{8.32}$$

The value of E_{cell} is obtained by potentiometer and E_G^o is known by working with a solution of known pH. Putting the value of E_{cell} and E_G^o in Eq. (8.32), pH of the given solution can be determined.

The **advantages** of glass electrode are as follows:

1. It can be used in the presence of strong oxidizing agents which interfere even with quinhydrone electrode.
2. It can also be used in the presence of metallic ions.
3. It is simple to operate for which it is commonly used in chemical and biological laboratories.

The **disadvantages** of glass electrode are as follows:

1. It can be used in solution of pH = 0 − 9. Electrodes of special glass can be used for measuring pH up to 12. But it cannot be used for a solution of pH >12.
2. Although glass membrane of electrode is very thin, yet its resistance is extremely high and hence potential cannot be measured by ordinary potentiometer.

Problem 12

A hydrogen electrode is immersed in a solution of pH = 3.5 and other half is SHE. Calculate the EMF of the cell if the two half-cells are connected by a salt bridge.

Solution

The cell can be represented as:

$$\text{Pt},H_2(1\text{ atm})|\ H^+(\text{unknown conc.})||H^+(1\text{M})|\ H_2(1\text{ atm}),\text{Pt}$$

The EMF of the cell is given by the following expression:

$$\begin{aligned} E_{\text{cell}} &= 0.0591 \text{ pH} \\ &= 0.0591 \times 3.5 = 0.207 \text{ V} \end{aligned}$$

Problem 13

The EMF of a cell consisting of hydrogen-electrode and normal calomel electrode is 0.664 V at 25°C. Calculate the pH of the solution containing hydrogen-electrode. Given that electrode potential of normal calomel electrode is 0.2802 V.

Solution

The cell can be represented as

$$\text{Pt}\,|\,\text{H}_2(1\text{atm})\,|\,\text{H}^+(\text{unknown conc.})\,||\,\text{KCl}(1\text{N}), \text{Hg}_2\text{Cl}_2(\text{s})\,|\,\text{Hg}$$

The half-cell reaction for hydrogen electrode is represented as:

$$\text{H}^+(\text{aq}) + e^- \rightleftharpoons \tfrac{1}{2}\text{H}_2(\text{g})$$

Nernst equation involving this half-cell reaction at 25°C can be written as:

$$E_{\text{H}^+/\text{H}_2} = E^{\text{o}}_{\text{H}^+/\text{H}_2} - \frac{2.303RT}{nF}\log\frac{[\text{H}_2]^{1/2}}{[\text{H}^+]}$$

where $E_{\text{H}^+/\text{H}_2}$ is the electrode potential of the hydrogen electrode present in the half-cell and $E^{\text{o}}_{\text{H}^+/\text{H}_2}$ is the electrode potential of standard hydrogen electrode, which is taken as zero. Substituting for R, T, F and n, we get

$$E_{\text{H}^+/\text{H}_2} = 0 - 0.0591\log\frac{1}{[\text{H}^+]} = -0.0591\text{ pH}$$

The EMF of the cell is calculated from the following relation:

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = 0.2802 - E_{\text{H}^+/\text{H}_2}$$

$$= 0.2802 - (-0.0591\text{ pH}) = 0.2802 + 0.0591\text{pH}$$

or

$$\text{pH} = \frac{E_{\text{cell}} - 0.2802}{0.0591}$$

$$= \frac{0.664 - 0.2802}{0.0591} = 6.494 \approx 6.5$$

Problem 14

Find out the pH of a solution in a quinhydrone half-cell, which is coupled with standard calomel electrode. The EMF of the combined cell was determined to be 0.123 V at 25°C. Given that $E^{\text{o}}_{SCE} = 0.2415$ V and $E^{\text{o}}_{Q/QH_2} = 0.6990$ V.

Solution

The cell is represented by

$$\text{SCE} \,\|\, \text{H}^+, \text{Q}, \text{QH}_2, \text{Pt}$$

where SCE is standard calomel electrode, Q is quinone and QH_2 is hydroquinone.
The EMF of the cell is given by:

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = E_{(\text{H}^+,\text{Q},\text{QH}_2)} - E_{\text{SCE}}$$

Electrode potential of quinhydrone electrode is given by:

$$E_{(\text{H}^+,\text{Q},\text{QH}_2)} = 0.6996 - 0.0591 \text{ pH}$$

So, $$E_{\text{cell}} = 0.6996 - 0.0591 \text{ pH} - 0.2415$$

or $$0.123 = 0.6996 - 0.0591 \text{ pH} - 0.2415$$

or $$\text{pH} = \frac{0.6990 - 0.123 - 0.2415}{0.0591}$$

$$= 5.65$$

Problem 15

EMF of the cell: SCE $\|$*AgCl(sat.)* $|$ *Ag(s) at 298 K was found to be equal to 0.2621 V. Calculate the solubility product of AgCl at this temperature. Given that* $E^{\text{o}}_{SCE} = 0.2415$ *V and* $E^{\text{o}}_{Cl^-,AgCl(s),Ag(s)} = 0.7991$ *V at 298 K.*

Solution

From the given values, we have

$$E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{cathode}} - E^{\text{o}}_{\text{anode}} = 0.7991 - 0.2415 = 0.5576 \text{ V}$$

At the cathode: $2\text{Ag}^+ + 2e^- \rightarrow 2\text{Ag}$

At the anode: $2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2e^-$

The overall cell reaction

$$2\,\text{Ag}^+ + 2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{Ag}$$

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - 0.0591 \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= 0.5576 - 0.0591 \log \frac{[\text{Hg}_2\text{Cl}_2][\text{Ag}]}{[\text{Ag}^+]^2[\text{Hg}]^2[\text{Cl}^-]^2}$$

Since AgCl is saturated, $[\text{Cl}^-] = 1$ mol/l. Substituting in above equation, we get

$$0.2621 = 0.5576 - 0.0591\ \log \frac{1}{[\mathrm{Ag}^+]^2}$$

$$0.2621 = 0.5576 - 0.0591\ (-\log\ [\mathrm{Ag}^+]^2)$$

$$0.2621 = 0.5576 + 0.0591\ (2\ \log\ [\mathrm{Ag}^+])$$

$$0.2621 = 0.5576 + 0.1182\ \log\ [\mathrm{Ag}^+]$$

$$\log\ [\mathrm{Ag}^+] = (0.2621 - 0.5576)\ /\ 0.1182 = -2.5$$

or $[\mathrm{Ag}^+] = 10^{-2.5}$ mol/l

In saturated solution $[\mathrm{Ag}^+] = [\mathrm{Cl}^-]$, so

$K_{sp} = [\mathrm{Ag}^+]\ [\mathrm{Cl}^-] = (10^{-2.5})^2 = 10^{-5}\ \mathrm{mol}^2/\mathrm{l}^2$

Problem 16

Determine the concentration of Cd^{2+} ions in the following electrochemical cell:

$$\mathrm{Fe}\,|\,\mathrm{Fe}^{2+}(0.1\,\mathrm{M})\,||\,\mathrm{Cd}^{2+}(x\,\mathrm{M})\,|\,\mathrm{Cd}$$

Given that $E_{cell} = -0.02$ V and $E^o = 0.04$ V at 298 K.

Solution

According to Nernst equation, for the cell reaction

$$\mathrm{Fe(s)} + \mathrm{Cd}^{2+}\mathrm{(aq)} \longrightarrow \mathrm{Fe}^{2+}\mathrm{(aq)} + \mathrm{Cd(s)}$$

$$E_{\mathrm{cell}} = E^{\mathrm{o}}_{\mathrm{cell}} - \frac{0.0591}{n} \log \frac{[\mathrm{Fe}^{2+}][\mathrm{Cd}]}{[\mathrm{Fe}][\mathrm{Cd}^{2+}]}$$

Substituting given values, we get

$$-0.02 = 0.04 - \frac{0.0591}{2} \log \frac{[0.1]}{[x]}$$

$$-0.06 = -\frac{0.0591}{2} \log \frac{[0.1]}{[x]}$$

$$2.03 = \log \frac{[0.1]}{[x]}$$

$$2.03 = -1 - \log[x]$$

$$3.03 = -\log[x]$$

$$\log x = -3.03$$

On taking antilog, we get $x = 0.00093$ M.

Concept Check

- What is calomel electrode? How is the pH of a solution measured by a saturated calomel electrode?
- What is quinhydrone electrode? How can pH of an unknown solution be determined using this electrode?
- A quinhydrone electrode is coupled with another electrode in a solution of pH 5.6. Find out the potential of the unknown electrode, given that $E_{\text{cell}} = 0.123$ V and $E^{\text{o}}_{\text{Quinhydrone}} = 0.699$ V.
- How is pH measured using a glass electrode? Discuss the advantages and limitations of the glass electrode.

8.9 Batteries

Conversion of chemical energy into electrical energy is the function involved in cells or batteries. A battery is a combination of cells either in series or parallel or both, in order to get the required amount of electrical energy. It is a portable source of electrical energy. In modern times, the words cell and battery are used interchangeably.

With the increased human activities and comforts, a number of battery-dependent appliances or goods have come into existence. Batteries are used in wrist watches, emergency sources of light (UPS), hearing aids, flashlight devices, electric calling bells, calculators, alarm signals, space vehicles and missile firing units.

There is a growing trend in the manufacture of consumer-friendly cells or batteries. In fact, not all the voltaic cells find commercial applications. The general criteria for any cell to be a commercial cell are that they should be cheap, light and portable; should have a long cycle life and high shelf life; should be a continuous and constant source of EMF over a long interval of time and should be a rechargeable unit. The galvanic cells used to form batteries can be classified as:

1. **Primary cells:** In these cells, the chemical energy is converted into electrical energy as long as the chemical components are active. Once the active chemical components are used up, they cannot be regenerated or reused. These cells are then not rechargeable.
2. **Secondary cells:** In these cells, the redox reaction that converts chemical energy into electrical energy can be reversed by passage of current. These cells can be recharged and reused. The electrical energy is stored in them in form of chemical energy and hence these are also known as storage cells. These cells behave as a galvanic cell during discharge (converting chemical energy into electrical energy) and as electrolytic cell during charging (converting electrical energy into chemical energy).

The basic components of a battery are:

1. **Anode:** It contains active materials which spontaneously take part in the oxidation reactions.
2. **Cathode:** It contains active materials which spontaneously take part in the reduction reactions.
3. **Electrolyte:** It helps in the migration of the ions leading to the generation of electrical energy.
4. **Separator:** It is a thin polymeric membrane which prevents the mixing of products formed at the electrodes. Usually, polypropylene and polystyrene separators are used.

Discharging and Charging of a Battery

A cell is a battery that is packed with active materials at anode and cathode. As soon as the anode and the cathode are connected to the load, redox reactions occur spontaneously. The electrons liberated at the anode flow to the cathode through the external wire and take part in the reduction reaction. This process in which spontaneous redox reaction occurs is called **discharging**.

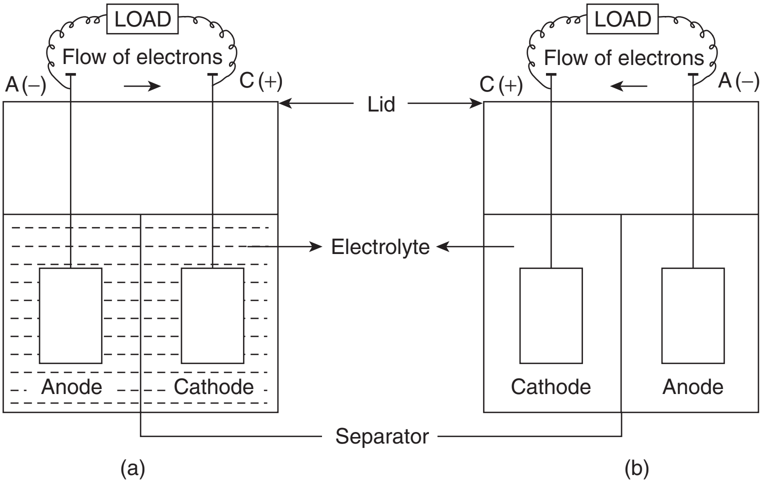


Figure 8 (a) Discharging and (b) charging processes in a battery.

During the discharging process as shown in Figure 8(a), active materials are converted into inactive materials. The cell becomes inactive once the active material is consumed. In case of secondary cells or batteries, the cell reaction is reversed if the external current is passed in the reverse direction. This process of conversion of an inactive material back into active materials in a cell is called **charging** as shown in Figure 8(b). It is a non-spontaneous process.

Characteristics of a Battery

Selection of a cell or battery depends on the conditions of working. In fact, cells or batteries are specifically designed for this purpose. The suitability of a cell or battery depends on the following characteristics:

1. **Voltage or EMF:** A good cell is one which offers large and almost constant EMF.
   - It depends on the change in free energy of the reaction.

   $$\Delta G = -nFE_{\text{cell}}$$

   Larger the change in free energy, higher will be the EMF.
   - According to Nernst's equation,

   $$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

   where $E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{R}} - E^{\text{o}}_{\text{L}}$.

   (a) Larger the potential difference between the electrodes, higher is $E^{\text{o}}_{\text{cell}}$ and hence E_{cell}.
   (b) As temperature increases, the EMF decreases.
   (c) As the value of [Products]/[Reactants] increases, EMF of the cell marginally decreases.

- A good cell or battery is one which has a flat discharge rate (constant EMF) (Figure 9).

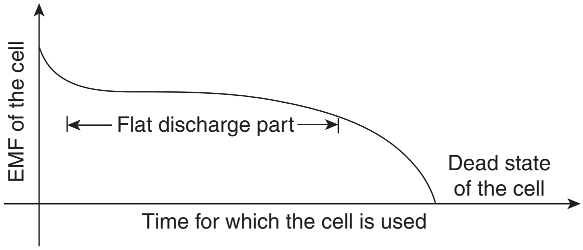


Figure 9 Flat discharge rate.

2. **Current:** It is a measure of the rate of discharge reactions of the cell. It depends on the amount of active materials. Higher the amount of active materials, longer will be the time for which EMF is generated.
3. **Current capacity:** It is defined as the amount of current generated in unit time. It is measured in terms of ampere-hour (A h) and depends on the discharge conditions. Capacity is inversely proportional to the average molar mass of the active materials. A good cell or battery should have higher current capacity.
4. **Power density:** It is a measure of the power generated in a cell per unit weight of the cell or battery.

$$\text{Power density} = \frac{\text{Amount of power generated in a cell}}{\text{Weight of the cell}} = \frac{iE_{\text{cell}}}{W}$$

   where i and E_{cell} are current and EMF generated in a cell, respectively. Lesser the weight of the cell, higher would be the power density.
5. **Energy density:** It is a measure of the energy available in the cell per unit weight of the cell.

$$\text{Energy density} = \frac{\text{Amount of energy generated in the cell}}{\text{Weight of the cell}} = \frac{i^2Rt}{W} = \frac{iE_{\text{cell(avg)}} \times t}{W}$$

   where i, R and t are the current generated by cell, resistance offered by the cell and time for which the current generated is measured. Always, cells or batteries with higher energy densities are preferred.
6. **Energy efficiency:** It is applicable only to secondary cells. During discharging, electrical energy is released while electrical energy is utilized when the cell is being charged. A good cell is that which liberates more electrical energy than it uses during charging process. The rates of electrical energy released and used in discharging and charging, respectively, is known as percentage energy efficiency. Thus,

$$\text{Percentage energy efficiency} = \frac{\text{Amount of electrical energy released during discharging}}{\text{Amount of electrical energy used during charging}} \times 100$$

7. **Cycle life:** It is applicable only to rechargeable (secondary) cells. The EMF of cell decreases during discharging. If it is followed by charging process, the amount of active materials in the cell increase and hence the EMF. The discharging and charging processes cannot be repeated perpetually. A discharging followed by charging is referred to as a **cycle**. The number of times it can be repeated is called **cycle life**. In other words, cycle life is defined as the number of times the discharging and charging operations can be alternated till such time it performs as designed.

   A good cell should have high cycle life. Sometimes, the cycle life would be lower than expected. It may be due to the following reasons.

- The active materials at the electrodes may whither off due to rapid charging conditions.
- There may be irregular deposition of the products during discharging. It may result in short circuiting.
- Due to overcharging, the corrosion may occur resulting in severing connections between the contact wire and the active materials.

8. **Shelf life:** The duration of storage under specified conditions at the end of which the cell still has the ability to deliver specified performance. A good cell or battery should possess a long shelf life.
9. **Self-discharge:** Sometimes, the discharge reactions may occur even though the cell is not in use. It is due to the local actions that occur in the cell. It is defined as the loss of active materials of the cell due to localized action on the electrode even when the cell is not in discharge mode. Longer the self-discharge, lower would be the shelf life.

Concept Check

- What are the criteria for a commercial battery?
- Explain the essential components of a battery.
- Explain the process of charging and discharging of a battery.
- What is meant by the energy efficiency of a battery?
- What are the reasons for the lowering of cycle life of a battery?

8.10 Classical Batteries

Primary Cells

Dry Cell

This cell, also known as Leclanche cell, consists of a cylindrical zinc container which acts as the anode. A graphite rod surrounded by a paste of manganese dioxide acts as the cathode. These are in contact with a thick paste of ammonium chloride and zinc chloride which acts as the electrolyte (Figure 10).

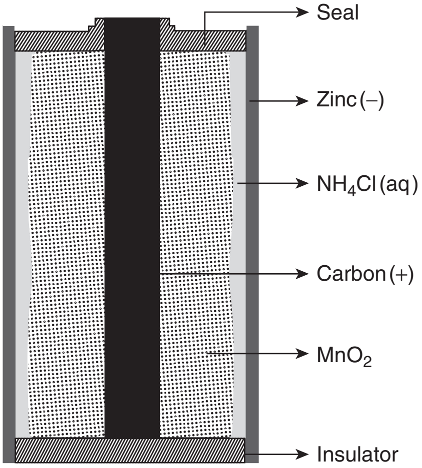


Figure 10 Leclanche cell.

The cell reactions are:

At the anode: $Zn \rightarrow Zn^{2+} + 2e^-$

At the cathode: $MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$

The overall cell reaction: $Zn + 2MnO_2 + H_2O \rightarrow Zn^{2+} + Mn_2O_3 + OH^-$

Some secondary reactions take place in the cells which do not contribute to the EMF of the cell as they do not occur at the electrodes. The hydroxyl ions generated at the cathode react with NH_4Cl to liberate ammonia which reacts with Zn^{2+} to form the complex $[Zn(NH_3)_4]Cl_2$. These processes disrupt the flow of current.

A dry cell develops a potential of 1.5 V and the voltage decreases with usage due to accumulation of products at the electrodes. Even when the cell is not in use, the lifetime of the dry cell is not indefinite because acidic NH_4Cl corrodes the zinc cathode. Dry cells are most commonly used batteries that find use in flashlights, radios, tape recorders, transistors, etc.

Alkaline Dry Cell

This cell is same in construction as the dry cell but modified to replace NH_4Cl as electrolyte by sodium hydroxide or potassium hydroxide, hence the name alkaline dry cell. Replacing NH_4Cl with NaOH/KOH prevents corrosion of zinc cathode since it does not dissolve in basic medium. The cell reactions are:

At the anode: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

At the cathode: $2MnO_2 + 2e^- + H_2O \rightarrow Mn_2O_3 + 2OH^-$

The overall cell reaction: $Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$

Mercury Cell

This cell, also known as Ruben–Mallory cell after the inventors, consists of amalgamated zinc powder that functions as the anode. The cathode comprises paste of mercuric oxide with some amount of graphite. A paste of zinc oxide and potassium hydroxide forms the electrolyte (Figure 11).

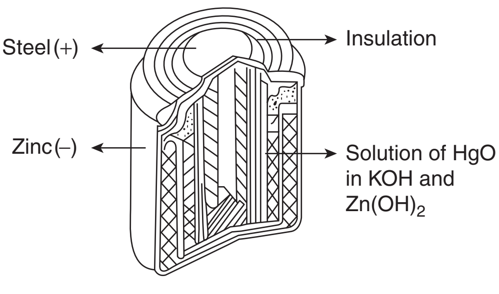


Figure 11 Mercury cell.

The cell reactions are:

At the anode: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

At the cathode: $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$

The overall cell reaction: $Zn + HgO \rightarrow ZnO + Hg$

The zinc cell develops a potential of 1.35 V. It is compact in size because the zinc anode can be compressed into pellet form; the cathode material, mercury oxide, is dense; and the electrolyte KOH is non-variant and thus required in minimal amount. It gives constant potential throughout its lifetime and shows good performance at high temperatures. It is however, expensive due to the high cost of mercury oxide. These cells are used in electronic watches, hearing aids, microphones, cameras, etc.

Silver Button Cell

This cell consists of silver oxide as cathode and zinc metal as the anode. These electrodes are separated by semi-permeable membranes and potassium hydroxide and sodium hydroxide is used as an electrolyte (Figure 12).

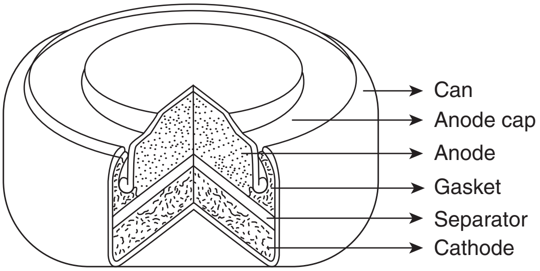


Figure 12 Silver button cell.

The cell reactions are:

At the anode: $\mathrm{Zn + 2OH^- \rightarrow ZnO + H_2O + 2}e^-$

At the cathode: $\mathrm{Ag_2O + H_2O + 2}e^- \rightarrow \mathrm{2Ag + 2OH^-}$

The overall cell reaction: $\mathrm{Zn + Ag_2O \rightarrow ZnO + 2Ag}$

The cell reaction shows that the amount of electrolyte does not change or is non-variant. The cell gives a voltage of 1.3–1.5 V, which remains fairly constant during the cell discharge. The cell is compact and finds use in electronic watches, hearing aids, pacemaker, etc.

Secondary (Storage) Cells

Lead Storage Cell (Lead–Acid Battery)

This cell, also known as acid storage cell, is the common automobile battery. Its present form is a variant of lead–acid accumulator first designed in 1859. Lead storage cell consists of lead grid filled with spongy lead which acts as the anode and a lead grid packed with lead oxide that acts as the cathode. A number of (generally six) such electrode pairs are dipped in sulphuric acid solution (20%) which acts as the electrolyte and these are separated by inert and porous partitions (Figure 13).

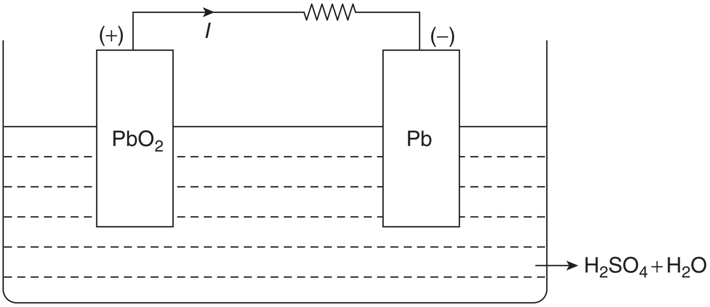


Figure 13 Lead–acid battery.

The cell reactions during discharge are:

At the anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

At the cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

The overall cell reaction: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

The cell reaction shows that the electrolyte H_2SO_4 is consumed during the reaction, so as the reaction proceeds, the concentration of H_2SO_4 decreases. Once the concentration of H_2SO_4 has fallen to a certain permissible level, the battery needs to be recharged by reversing the discharge reaction. For this, an external potential higher than the cell potential is applied. The cell then operates like an electrolytic cell and the $PbSO_4$ deposited on the electrodes is reverted to Pb and PbO_2 by the following charging reactions:

At the anode: $PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

At the cathode: $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$

The overall cell reaction: $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$

The cell reactions show that the concentration of H_2SO_4 increases during recharging of the cell. The potential developed by each electrode pair is about 2 V and higher potential can be obtained by connecting a number of electrode pairs in series. These batteries find extensive use as automobile batteries. Besides these, it is used for electrical supply in trains, hospitals, etc.

Nickel–Cadmium Cell

This cell, also known as alkaline storage battery, consists of anode grid which contains spongy cadmium with cadmium hydroxide. The cathode grid contains nickel oxyhydroxide along with small amounts of graphite and other compounds. A concentrated solution of potassium hydroxide acts as an electrolyte (Figure 14).

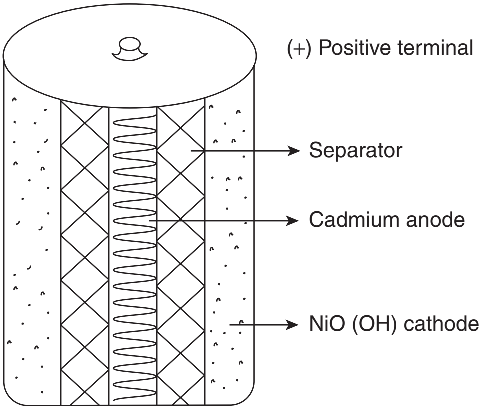


Figure 14 Nickel–cadmium cell.

Cell reactions during discharging are:

At the anode: $Cd + 2OH^- \rightarrow Cd\,(OH)_2 + 2e^-$

At the cathode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$

The overall cell reaction: $Cd + 2NiO(OH) + 2\,H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$

As the reaction proceeds, the products $Ni(OH)_2$ and $Cd(OH)_2$ stick to the surface of the electrode. The cell can be recharged by reversing the reactions. Cell reactions during charging are:

At the anode: $2Ni(OH)_2 + 2OH^- \rightarrow 2NiO(OH) + 2H_2O + 2e^-$

At the cathode: $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$

The overall cell reaction: $2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + Cd + H_2O$

This cell gives potential of about 1.4 V. It can be made into compact button cell type battery and finds use in pocket calculators, electronic flash lights, emergency lights, portable electronics, toys, etc.

Concept Check

- Explain the working of a dry cell along with the redox reactions taking place.
- Explain the construction and working of lead acid battery.
- Separator is not required in a lead acid battery. Justify the statement.
- Explain the functioning of nickel–cadmium battery.

8.11 Modern Batteries

Metal–Air Batteries

Metal–air batteries are the batteries which breathe air, that is, they use oxygen directly from the air to bring about the electrochemical reaction. These are basically alkaline batteries in which the cathodic active material is not stored in the cell. Of the several types available, zinc–air batteries are more popular. They were commercialized in 1977.

The zinc–air battery (Figure 15) is constructed in the following way:

1. Anode is composed of granulated zinc powder mixed with an aqueous solution 30% KOH and a gelling agent to immobilize the material.
2. Cathode is composed of mixture of carbon and the catalyst (oxides of manganese), and a gelling agent held on a nickel-coated steel matrix. Several hydrophobic, gas permeable, thin layers of teflon are provided to steady the air entry.
3. Electrolyte contains 30% KOH.
4. There is also a vent for the entry of air or O_2 into the cell.
5. The container is made of glass and has a separator made of nylon.

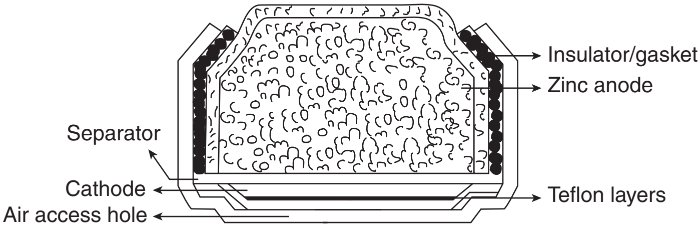


Figure 15 Zinc–air battery.

The cell is represented as:

$$Zn \,|\, 30\%\ KOH \,|\, Air, C$$

The reactions involved in the cell are:
At the anode:

$$\begin{array}{l} \mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e^- \\ \mathrm{Zn}^{2+} + 2\mathrm{OH}^- \rightarrow \mathrm{ZnO} + \mathrm{H_2O} \\ \hline \mathrm{Zn} + 2\mathrm{OH}^- \rightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2e^- \\ \hline \end{array}$$

At the cathode:

$$\mathrm{H_2O} + \tfrac{1}{2}\mathrm{O_2} + 2e^- \rightarrow 2\mathrm{OH}^-$$

The overall cell reaction:

$$\mathrm{Zn} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{ZnO}$$

The battery offers an EMF of 1.25–1.35 V.
The characteristics of zinc–air batteries are as follows:

1. These are light and have high energy density.
2. These relatively eco-friendly and have unlimited capacity.
3. These suffer from low shelf life. Still, they are known for low energy cost.

These batteries find application in hearing aids, several medical devices and military radio receivers.

Nickel–Metal Hydride Batteries

These batteries are also alkaline, rechargeable batteries and were commercialized in 1990. Their construction (Figure 16) is done as follows:

1. Anode of the cell is composed of metal hydrides like MH and MH_2. Active hydrogen storage alloy like $LaNi_5$ are pasted on a very thin, highly porous nickel sheet.
2. Cathode is composed of NiO(OH) is pasted on a very thin, highly porous nickel sheet.
3. Electrolyte used is aqueous potassium hydroxide.
4. Separator contains a thin layer of polypropylene.
5. All the components are housed in a glass container.

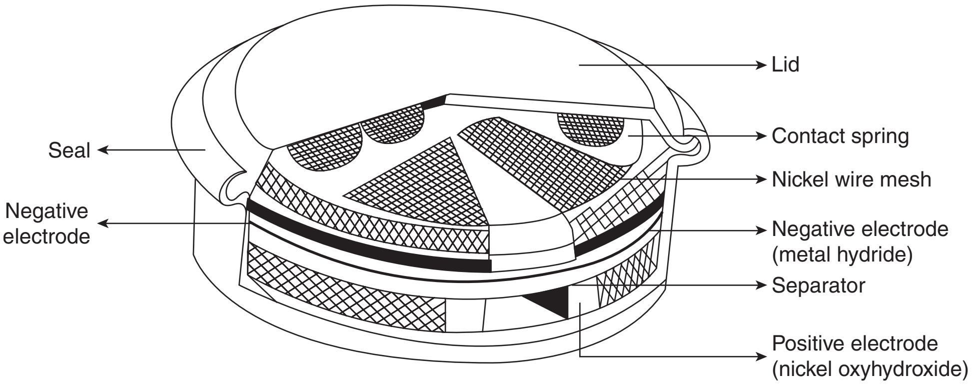


Figure 16 Nickel–metal hydride battery.

The cell representation is as follows:

$$MH_2 \,|\, KOH(5\ M) \,|\, Ni(OH)_2, NiO(OH)$$

The reactions involved in the cell are:

At the anode: $MH_2 + 2OH^- \rightarrow M + 2H_2O + 2e^-$

At the cathode: $NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

The overall cell reaction is

$$\begin{array}{l} MH_2 + 2OH^- \rightarrow M + 2H_2O + 2e^- \\ \underline{(NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-) \times 2} \\ NH_2 + 2NiO(OH) \rightarrow M + 2Ni(OH)_2 \end{array}$$

The battery offers an EMF of 1.3 V.

The characteristics of nickel–metal hydride batteries are as follows:

1. They have long shelf life and cycle life.
2. They have high capacity and rapid recharge capability.
3. They have poor charge detention capacity.

These batteries find application in laptop computers, cellular phones as well as automobiles.

Lithium Batteries

Lithium is a light metal with low electrode potential and good conductivity. It is, therefore, a good material for batteries, and can be expected to have high potential and high energy density. The group of batteries where lithium is used as an anode are known as lithium batteries and they were commercialized in 1990. A large number of lithium batteries are available which have lithium as anode but differ in choice of cathode and electrolyte. These may also be classified as primary or secondary. The most well-known of lithium batteries, lithium–manganese dioxide cell is discussed here.

The construction of Li–MnO_2 battery is as follows:

1. Anode is composed of lithium.
2. Cathode is composed of heat treated MnO_2.
3. Electrolyte contains a mixture of LiCl, LiBr, $LiAlO_4$ and $LiClO_4$ dissolved in organic solvents like propylene carbonate and is 2-dimethoxyethane.

The cell reactions are as follows:

At the anode: $Li \rightarrow Li^+ + e^-$

At the cathode: $MnO_2 + Li^+ + e^- \rightarrow Li\overset{III}{Mn}O_2$

The overall cell reaction is: $Li + MnO_2 \rightarrow Li\overset{III}{Mn}O_2$

The battery offers an EMF of 3.0 V.

These batteries have the following characteristics:

1. The batteries are light in weight and compact.

2. They are known for low maintenance and have high energy density.

These batteries find application in memory backups, automatic cameras and calculators.

Concept Check

- Zinc–air battery has high energy density. Explain.
- Discuss the construction and working of nickel–metal hydride battery.
- Lithium can be the best component of a battery. Substantiate.

8.12 Fuel Cells

Conventionally energy is obtained by the combustion of the fossil fuel. The conversion into electrical energy involves a number of steps and there is loss of energy at every step. The efficiency of the process is around 40%. There is also a viable way of converting the chemical energy of fuel directly into electrical energy through catalytically activated redox reactions. Such devices are called **fuel cells**. Even though fuel cells were first demonstrated by Sir William Grove in 1839, they became popular only after NASA used them in their space ships (1950s). In other words, fuel cells are galvanic cells in which the electrical energy is directly derived from the redox reactions of the fuel.

Comparison with Conventional Galvanic Cells

Fuel cells differ from the conventional galvanic cells in the following aspects:

1. They consist of two catalytic electrodes.
2. The reagents used are fuel and oxidant.
3. The fuel and oxidant are not stored in the cell. They are stored outside and supplied as and when required.
4. No pollutants and hence fuel cells are environmentally friendly.
5. No toxic species are formed in a fuel cell.
6. They do not need charging.

Advantages and Limitations

Distinct advantages of fuel cells are:

1. They offer high energy conversions (almost 75%).
2. These cells have high energy density.
3. These cells use inexpensive fuels.

Fuel cells suffer from a few limitations:

1. The electrodes used are either Pt, Ag or the alloys of noble metal which are prohibitively costly.
2. The power generated is moderate.

Cell Representation

The representation of the fuel cell is:

Fuel | Electrode | Electrolyte | Electrode | Oxidant

The chemical reactions involved at the electrodes are:

At the anode: Fuel → Oxidation product + ne^-

At the cathode: Oxidant + ne^- → Reduction product

The overall cell reaction: Fuel + Oxidant → Oxidizing product + Reduction product

The frequently used fuels are hydrogen, methanol, ethanol, hydrazine, formaldehyde, carbon monoxide and alkane. The oxidants could be pure oxygen or air.

Hydrogen–Oxygen Fuel Cell

This fuel cell combines hydrogen and oxygen to produce electricity, heat and water. It converts chemical energy to electrical energy and thus can be compared to a battery. The only difference being that as long as hydrogen is supplied, it continues to produce electricity.

Design and Working

The whole setup consists of chambers (Figure 17). The first chamber serves as an inlet for hydrogen, while the second one serves as an inlet for oxygen. There are two electrodes: Hydrogen passes over the anode and oxygen passes over the cathode. In the middle, there is a proton exchange membrane separating the two electrodes from one another, where these two gases can interact with each other. The electrolyte separating the two electrodes is an ion-conducting material. When electricity is applied, the following reactions take place at the two electrodes:

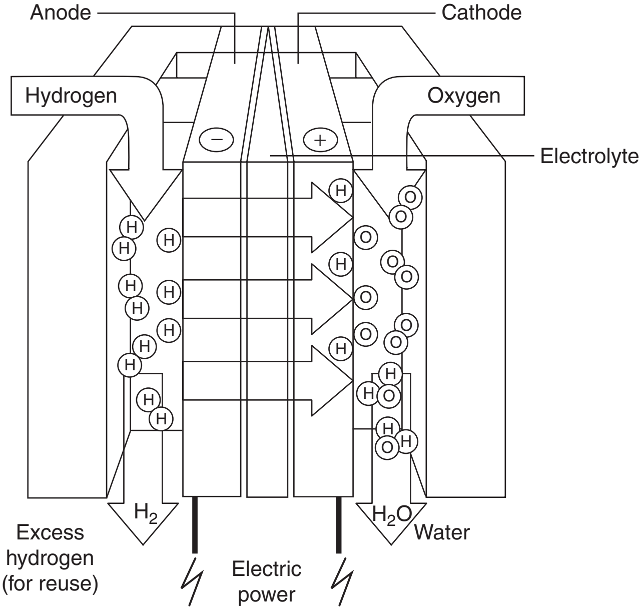


Figure 17 A block diagram of hydrogen–oxygen fuel cell.

At the anode: $2H_2 \rightarrow 4H^+ + 4e^-$

At the cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

The overall cell reaction: $2H_2 + O_2 \rightarrow 2H_2O$

The water is released in the fourth chamber. The anodic reaction gives protons and electrons. These are separated and hydrogen ions are allowed to pass through the electrolyte to the cathode while the electrons travel via an external circuit as direct current to power electrical devices. In the cathode, hydrogen ions combine with oxygen to form water along with the heat, thus completing the circuit.

Advantages and Limitations

There are a lot of benefits of using hydrogen as a fuel.

1. It just emits water vapor and no other harmful chemicals to the environment.
2. The efficiency shown is as high as about 75%.
3. Hydrogen is the lightest element and provides a lot of energy, and also it can be transported easily to places where required.
4. Hydrogen fuel can replace the use of batteries and causes less noise pollution.

There are also some limitations:

1. Hydrogen is explosive.
2. For very good efficiency, it turns out to be very expensive, and even the initial research which is to be carried out costs a lot of money.
3. Hydrogen is actually gas, so a large investment of cost and energy is required to compress it into liquefied form.
4. While using these fuel cells in an automobile, a high pressure is created inside the engine, which is quite risky.
5. Another big disadvantage would be that since hydrogen is never present as it is, but always in combined form with either oxygen or some other element, it needs to be separated first.

Types of Fuel Cells

The fuel cells can be classified into different types based on the fuel and electrolytes used:

1. **Alkaline fuel cells:** These are low-temperature fuel cells (80°C) using concentrated KOH as the electrolyte. Usually, alkali is preferred in H_2–O_2 fuel cell because the reduction of oxygen in alkaline medium in very quick. Higher alkanes are not used in these cells. The CO_2 formed, blocks the porosities as carbonates, and efficiency of the cell is decreased. Normally, Pt and Ag are used as catalysts.
2. **Methanol–oxygen fuel cell:** These cells can be used either in alkaline or in acidic medium. Presently, the most preferred electrolyte is the acidic medium. Methanol is a good fuel as it has low carbon content and has easily oxidizable –OH group present in it. The Pt electrodes are usually used and 3.7 M H_2SO_4 is used as the electrolyte.

   The cell reactions are:

   At the anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

At the cathode: $\left[\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O\right] \times 3$

The overall cell reaction is

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

These cells have an EMF of 1.2 V. Methanol–oxygen fuel cells find applications in military equipment. These applications include power for soldier-carried equipment, battery chargers, autonomous power for test and training instruments

3. **Phosphoric acid fuel cells (PAFCs):** These are moderate-temperature fuel cells (160–220°C). Phosphoric acid is used as the electrolyte, as it is a better conductor at high temperature.
4. **Molten carbonate fuel cells (MCFCs):** These operate at about 650°C. Molten carbonates are the electrolytes. H_2 or CO is the fuel, while O_2 is the oxidant. As high temperature is employed, fairly less expensive catalysts like Ni or NiO are used. The anode comprises porous Ni with1–2% chromium and the cathode comprises porous Ni with 1–2% Li.

   The reactions in the cell are:

Electrode	*For H_2*	*For CO*
At the anode	$H_2CO_3 \rightarrow H_2O + CO_2 + 2e^-$	$CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^-$
At the cathode	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$
The overall cell reaction	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$CO + \frac{1}{2}O_2 \rightarrow CO_2$

   The EMF generated is around 0.9 V. This cell is used in chloroalkali industries.
5. **Solid oxide fuel cells (SOFC):** These cells operate at temperature (650–1000°C). Special feature of these cells are solid electrolyte is used. Extent of corrosion of the container is minimum. The solid oxide helps in the migration of the prime species, that is, O^{2-}.
   - Anode is porous electrode coated with Co and ZrO_2.
   - Cathode contains $LaMnO_3$ doped with strontium.
   - Precaution should be taken while using completely non-porous solid oxide as the electrolyte. Zirconia (ZrO_2) doped with about 10 mol% of yttria (Y_2O_3) is generally used.
   - The fuel used is H_2 or CO.

   The cell reactions are as follows:

Electrode	*For H_2*	*For CO*
At the anode	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$CO + O^{2-} \rightarrow CO_2 + 2e^-$
At the cathode	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$
The overall cell reaction	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$CO + \frac{1}{2}O_2 \rightarrow CO_2$

SOFCs are used in situations where large amount of heat is required.

6. **Solid polymer electrolyte fuel cells (SPEFCS):** It is a relatively new and fast-growing technology. These cells operate at low temperatures. Solid polymer membranes capable of H^+ migration are used. Teflon-based ion-exchange membranes containing sulphonic acid groups ($-SO_3H$) are frequently used. The cell is compact as the membrane can be very thin. Porous carbon electrodes impregnated with Pt are used as electrodes. H_2 and O_2 are normally used as fuel and oxidant, respectively.
   The cell reactions are:

   At the anode: $H_2 \rightarrow 2H^+ + 2e^-$

   At the cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

   The overall cell reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

   The membrane serves two important purposes: (a) provides ionic migration and (b) separates anodic and the cathodic compartments so that the species do not get mixed.
7. **Microbial fuel cells (MFCs):** A microbial fuel (biological fuel) is a bio-electrochemical system. It is device that converts chemical energy into electrical energy by the catalytic action of microorganisms. A typical MFC consists of anodic and cathodic compartments separated by a cationic membrane. In the anodic compartment, fuel is oxidized by microorganism generating H^+ and electrons. Carbohydrates are the common fuels used.

$$C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^-$$

   Most of the microbial cells are electrochemically inactive. Transfer of electrons to the electrode is facilitated by mediators. Methylene blue, humic acid, thionine are usually used as mediators. These are expensive and toxic too. Mixture of mediator and microorganism (yeast cells) are mixed together in a solution. Suitable substrate (glucose) is added. The mixture is sealed in a chamber, providing anaerobic condition. An electrode is placed in the solution which acts as the anode. Mediators take up electrons and move towards the anode.

   In the second chamber, there will be another solution containing oxidizing agent and a cathode. Oxidizing agents take up electrons at cathode. The two chambers are connected by cation exchange membrane.

   The salient features of MFCs are as follows:
   - The electrodes are generally very thin (approximately 7 μm).
   - They operate in mild conditions (20–40°C, pH is around 7).
   - Waste water especially of brewery industries can be used.
   - These cells generate clean water.

Concept Check

- Fuel cells are the future source of electrical energy. Explain.
- How does a fuel cell differ from a galvanic cell?
- Write the reactions involved in the working of hydrogen-oxygen fuel cell. Why is water removed continuously from this cell?
- Discuss the working of a methanol-oxygen fuel cell?
- Alkaline fuel cells do not use compounds with higher carbon content. Justify.

8.13 Corrosion in Metals and Alloys

Metals are thermodynamically unstable and found abundantly in nature, so that they require large amounts of energy to get converted into useful engineering materials. Thus, the metals requiring more energy have a greater tendency to corrode, whereas those metals requiring less energy have a lower tendency to corrode. Examples of the former include magnesium, zinc, aluminum and steel; whereas examples of the latter include gold, silver and platinum. Corrosion is a spontaneous slow chemical interaction of metal or alloy with its environment, resulting in the formation of one of its compounds such as oxide, hydrated oxide, carbonate, sulphide, sulphate, etc. Extraction of metals from their ores is an endothermic process. Pure metals, being highly energetic, have natural tendency to revert back to their combined states.

$$\text{Metal ores} \underset{\text{Corrosion}}{\overset{\text{Metallurgical extraction}}{\rightleftharpoons}} \text{Metal}$$

Hence, corrosion can be defined as the destruction of metals or alloys by the environment through chemical or electrochemical changes.

Causes of Corrosion

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most familiar example of corrosion is rusting of iron exposed to the atmospheric conditions.

$$2\text{Fe(s)} + \frac{3}{2}\text{O}_2\text{(g)} + x\text{H}_2\text{O(l)} \rightarrow \underset{\text{(Chemical composition of rust)}}{\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O(s)}}$$

Corrosion of metals occurs either by direct chemical attack or by electrochemical attack on the metal by the corrosive environment.

Effects of Corrosion

The effects of corrosion are many and varied. These effects are more pronounced than the simple loss of metal as they affect the safe and efficient functioning of equipments or structures. Even if the loss of metal due to corrosion is small, still it may be required to replace the expensive parts of the equipment. The major harmful effects of corrosion can be summarized as follows:

1. Loss of metal or reduced thickness: This reduced thickness may lead to lack of mechanical strength, leading to structural breakdown. Sudden structure collapse or breakdown may cause hazards or injuries to those working near the site of the structure (e.g., bridges, cars, aircrafts). Loss of metal in localized areas gives a crack-like appearance to the structure. Hence considerable weakness may result from even a small amount of metal loss.
2. Time is lost in making available the required parts required for constructing the industrial equipment.
3. The value of the goods is reduced owing to degraded appearance.
4. The fluids stored in pipes or storage tanks get contaminated due to chemical reactions (e.g., beer gets cloudy when small quantities of heavy metals are released by corrosion).

5. Important surface properties of metals are affected. These properties include frictional, bearing properties, ease of fluid flow, electrical conductivity, surface reflectivity and heat transfer. There is loss of technically important surface properties of a metallic component.
6. Mechanical damage to valves, pumps, etc., or blockage of pipes by solid corrosion products.

Types of Corrosion

Dry Corrosion (Direct Chemical Attack)

Dry corrosion involves direct attack of atmospheric gases on metal in the absence of moisture liquid phase, that is, conducting (aqueous) medium. The corrosive media include vapors, gases, etc. The example of dry corrosion is the reaction between metal and oxygen (atmosphere) at elevated temperatures in perfectly dry conditions.

Compared to other gases and chemicals, it is found that oxygen is mainly responsible for the corrosion of most metallic substances. Accordingly, corrosion on metallic surface is due to direct reaction of atmospheric gases such as oxygen; halogens; oxides of sulphur, nitrogen; hydrogen sulphide and fumes evolved due to chemical reactions with metal. There are three main types of dry corrosion.

1. **Oxidation corrosion (reaction with oxygen):** Some metals directly react with oxygen in the absence of moisture. For instance, alkali and alkaline earth metals react with oxygen at room temperature to form corresponding oxides, while others react with oxygen at higher temperature. Noble metals such as Ag, Au and Pt are not easily oxidizable and form an unstable layer which decomposes soon after its formation, thereby preventing further corrosion.

   The metal–oxide layer formed on the metal's surface protects the metal against chemical action of corrosive agents. Any diffusion through this layer of either the metal or the oxide can lead to further corrosion. Thus, this layer plays an important role in controlling corrosion. Stable oxides of Pb, Al and Sn inhibit further corrosion by forming a stoichiometric, non-porous, strong-adhering oxide films.

   However, in case the oxide film is porous, atmospheric gases passing through the pores will react with the metal, and the process of corrosion continues till the entire metal is converted into its oxide. This type of layer is formed by alkali and alkaline earth metals. Molybdenum forms a volatile oxide film of MoO_3 which accelerates corrosion.
2. **Corrosion by other gases such as Cl_2, SO_2, H_2S, NO_x:** In dry atmosphere, these gases react with metal and form corrosion products, which may be protective or non-protective. Dry Cl_2 reacts with Ag and forms AgCl which is a protective layer, while $SnCl_4$ is volatile. In petroleum industries at high temperatures, H_2S attacks steel forming FeS scale which is porous and interferes with normal operations.
3. **Liquid metal corrosion:** In several industries, molten metal passes through metallic pipes and causes corrosion due to dissolution or internal penetration. For example, liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.

Wet Corrosion (Electrochemical Theory of Corrosion)

Wet corrosion usually occurs in conducting liquid (aqueous) phase. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution. In other words, wet corrosion involves electrochemical attack on metals in aqueous environments. This corrosion is more prevalent than dry corrosion.

According to the electrochemical theory of corrosion, the corrosion of a metal like iron exposed to the environment may be thought of as a three-step process.

1. Formation of large number of galvanic cells, that is, the development of anodic and cathodic regions on the same metal (Figure 18). The electrons released at the anode are absorbed at cathode.
2. Corrosion (oxidation) takes place at the anodic region.
3. Reduction of O_2 (air) in presence of water to hydroxyl {OH^-} ions takes place at cathodic region.

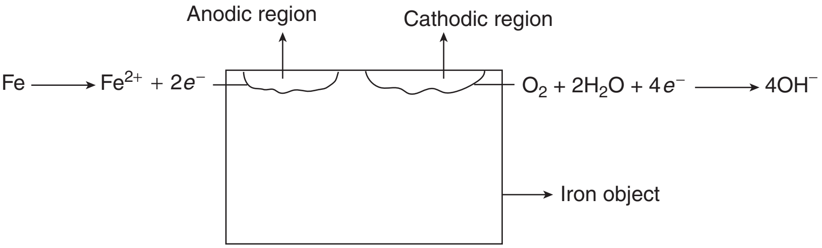


Figure 18 Galvanic cell.

The reactions involved in the galvanic cell are as follows:

1. **Anodic reaction:** Metal undergoes oxidation (corrosion) with positive release of electrons:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

At the cathodic region, electrons are absorbed and cause reduction of constituents.

2. **Cathodic reactions:** These reactions are dependent on the constituents of the corrosion medium. There are three possible ways in which reduction takes place:
   - If the solution is aerated and almost neutral, oxygen is reduced in presence of H_2O to OH^- ions.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

   - If the solution is deaerated and almost neutral, H_2 is liberated along with OH^- ions.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

   - If the solution is deaerated and acidic, H^+ ions are reduced to hydrogen gas

$$2H^+ + 2e^- \rightarrow H_2$$

3. The metal ions formed at the anode combine with hydroxyl ions and form the corresponding metallic hydroxide $Fe(OH)_2$, which further gets oxidized to hydrated ferric oxide {rust}.

$$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2$$

$$2Fe(OH)_2 + O_2 + (x-2)H_2O \rightarrow \underset{\text{(Rust)}}{Fe_2O_3 \cdot x\,H_2O}$$

   - In the presence of limited oxygen, black rust is formed as follows:

$$3Fe(OH)_2 + \tfrac{1}{2}O_2 \rightarrow \underset{\text{(Black rust)}}{Fe_3O_4 \cdot 3H_2O}$$

Differences between Dry Corrosion and Wet Corrosion

The difference between the dry corrosion and wet corrosion are elucidated in Table 2.

Table 2 Comparison between dry corrosion and wet corrosion

Dry Corrosion	*Wet Corrosion*
Involves direct attack of atmospheric gases on metal in the absence of moisture liquid phase	Involves electrochemical attack on metals in aqueous environments
Less prevalent	More prevalent
The corrosive media include vapors, gases, etc.	The corrosive media is conducting liquid (aqueous) phase
It is of three types: Oxidation corrosion, corrosion by other gases such as Cl_2, SO_2, H_2S, NO_x and liquid metal corrosion	It is of three types: differential metal corrosion, differential aeration corrosion and crevice corrosion

Types of Electrochemical Corrosion

Differential Metal Corrosion (Galvanic Corrosion)

Differential metal corrosion occurs when two dissimilar metals are in contact with each other in a corrosive environment. The metal with low reduction potential (anode) undergoes oxidation (corrosion), while metal with high reduction potential (cathode) undergoes reduction. The greater the electrode potential difference, the higher is the corrosion rate. Thus, it is the anodic metal that always undergoes corrosion and cathodic metal is unattacked.

EXAMPLE 1

Consider a bimetallic couple of iron and copper (Figure 19). The electrochemical series is as follows: Mg (−2.52 V); Zn (−0.76 V); Fe (−0.44); Cu (0.34 V) and Ag (0.80 V). As observed, iron is placed above copper in electrochemical series. Therefore, iron is anodic to copper, that is, iron acts as anode and undergoes corrosion, whereas copper acts as cathode and remains unattacked. The reactions involved in the galvanic cell are as follows:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^-$$

$$\tfrac{1}{2}\mathrm{O}_2 + \mathrm{H_2O} + 2e^- \rightarrow 2\mathrm{OH}^-$$

$$2\mathrm{Fe}^{2+} + 4\,\mathrm{OH}^- \rightarrow 2\mathrm{Fe(OH)}_2$$

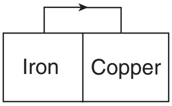


Figure 19 Bimetallic couple of iron and copper.

EXAMPLE 2 Consider a bimetallic sample of iron and zinc as shown in Figure 20.

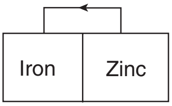


Figure 20 Bimetallic couple of iron and zinc.

As zinc is placed above iron in the electrochemical series, zinc is anodic to Fe. Therefore, zinc undergoes corrosion. Hence, we find that iron corrodes in contact with copper or silver, whereas zinc and magnesium corrode in contact with iron. The rate of differential metal corrosion depends upon the potential difference between the two metals; higher the difference, faster is the rate of corrosion.

EXAMPLE 3 Consider another bimetallic couple of steel and copper as shown in Figure 21.

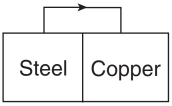


Figure 21 Bimetallic couple of steel and copper.

Steel is anodic in nature thus undergoes corrosion (as iron is above copper in the electrochemical series). The rate of corrosion depends on the potential difference between the two metals (materials).

Other examples of differential metal corrosion (galvanic corrosion) include the following:

1. Buried iron pipeline connected to zinc bar.
2. Steel pipe connected to copper plumbing.
3. Steel propeller shaft in bronze bearing.
4. Zinc coating on mild steel.
5. Lead–tin solder around copper wires.

Preventive Measures

1. Placing a thin layer of an insulator between two metals or materials.
2. Selecting materials having very less potential difference.

Differential Aeration Corrosion (Concentration Cell Corrosion)

Differential aeration corrosion occurs when a metal is exposed to differential air concentrations or oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as cathodic region and the part of the metal exposed to lower oxygen concentration acts as anodic region.

EXAMPLE 4 Consider a plate of pure iron which is partially immersed in an aerated solution of sodium chloride (Figure 22).

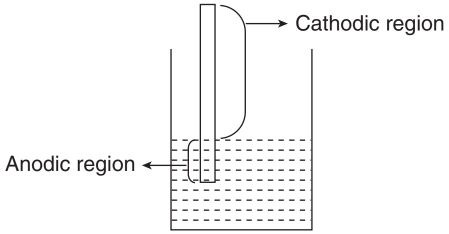


Figure 22 Pure iron partially immersed in an aerated solution of NaCl.

Since cathodic reaction requires oxygen, the part of the metal exposed to higher oxygen concentration always acts as the cathodic region. The portion of the metal immersed in NaCl is anodic region. The reactions involved are as follows:

Anodic reaction at the lower immersed portion of metal: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$

Cathodic reaction near the water surface: $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^-$

The examples of differential aeration corrosion include:

1. Half-immersed iron plate in aqueous solution.
2. Steel pipe carrying any liquid exposed to atmosphere.
3. Ocean going ships.
4. Steel storage tanks.

Preventive Measures

1. Using metallic coating, electroless plating or chemical conversion methods.
2. Maintaining the material's own protective film.
3. Controlling the chemistry of fluids and using inhibitors.

Waterline Corrosion

Waterline corrosion is a case of differential aeration corrosion. Ocean going ships and water storage steel tanks undergo this type of corrosion (Figure 23). The metal portion just below the waterline is more anodic to portion above the water line. Therefore, the metal just below the waterline undergoes corrosion.

Waterline corrosion is common in water-lifting pipes under water. Ocean going ships also suffer from differential aeration corrosion. Ships sunk under water for several years do not undergo corrosion. For the portion of the ship sunk under water, the difference in O_2 concentration between the top and bottom portions of the ship is negligibly small. Thus, the ship is exposed to almost uniform concentration of air and does not undergo differential aeration corrosion.

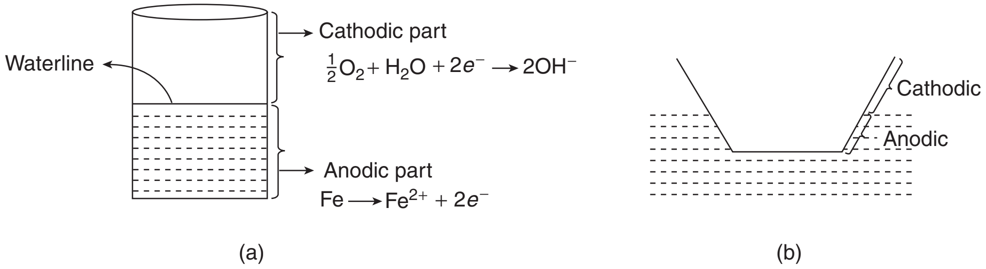


Figure 23 Waterline corrosion: (a) Water storage tank and (b) ocean going ship.

Crevice Corrosion

Crevice corrosion is often associated with a small volume of stagnant solution or electrolyte trapped in crevices of joints, rivets, bolts, gasket surfaces, lap joints, nuts, washers or in surface deposits. This corrosion occurs when oxygen cannot penetrate a crevice, leading to set up of a differential aeration cell. Corrosion occurs rapidly in the area with less oxygen. Also, consider the corrosion occurring when the surface of a painted metal is scratched. The scratched portion would act as a small anode, while the rest of the part would act as cathode, thus forming a local differential aeration cell.

Mechanism

In general, crevice corrosion occurs rapidly in the area with less oxygen. Increase in acidity and chloride content of crevice solution initiates passive film breakdown process, and thereby enhances the rate of corrosion reaction. Finally, corrosion propagation continues leading to further deterioration of the material.

The Fontana and Greene model describes crevice corrosion mechanism. This model consists of four stages.

Stage 1: Corrosion occurs normal both inside and outside the crevice with the following reactions:
Anode reaction: $M \rightarrow M^{n+} + ne^-$
Cathode reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.
The positively charged metallic ions are electrostatically counterbalanced by OH^- ions.

Stage 2: The cathode reaction inside the crevice consumes most of the available oxygen.

Stage 3: The Cl^- and OH^- ions diffuse into the crevice to maintain minimum potential energy, thus forming the metal chloride. Hydrolysis of metal chloride lowers pH and

$$MCl + nH_2O \rightarrow M(OH)_n + nHCl.$$

Stage 4: More M^{n+} ions attack more Cl^- leading to lower pH inside crevice. This accelerates the dissolution of metal and more M^{n+} ions will be produced that will further lower the pH.

Preventive Measures

1. Increasing resistance by using alloys that have high percentage of chromium, molybdenum and/or nitrogen.
2. Design and fabricate to avoid crevices.
3. Frequently inspecting for inadvertent crevices and closing crevices by continuous welding, caulking or soldering.

Pitting Corrosion

Pitting corrosion involves localized attack usually in chloride medium. This corrosion arises when a small portion of the metallic surface is either defective (with cracks) or occupied by dust/scale/sand/water drop.

Mechanism

Figure 24 shows the mechanism of pitting corrosion of iron surface in the chloride medium. The metal below the dust (deposit particle) is exposed to lower O_2 concentration and undergoes corrosion. Once a pit is formed, the rate of corrosion increases. The accelerated corrosion takes place below the deposit because of small anodic area and large cathodic area.

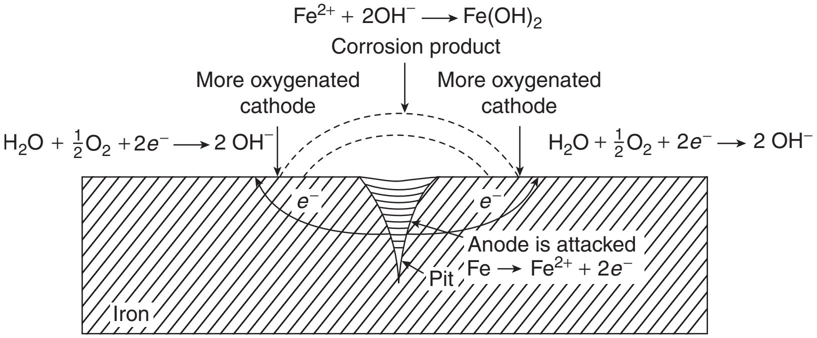


Figure 24 Pitting corrosion on the surface of iron.

Preventive Measures

1. Preparing surfaces with best possible finish. Mirror-finish resists pitting best.
2. Removing all contaminants, especially free-iron by passivation.
3. Designing and fabricating to avoid trapped and pooled liquids.

Other Types of Corrosion

1. **Stress corrosion:** Mechanical forces within the metal bring about stress corrosion. The internal stress of metal arises when the metal is subjected to mechanical operations such as pressing, hammering, bending, welding or riveting. The stress can also be external stress that acts on the metal during service conditions. The metal atoms under stress are always at higher energy levels as compared to stress-free atoms. The stressed part of the metal, therefore, becomes more reactive than the stress-free part. As a result, a galvanic cell is formed with the stressed part acting as anode, and stress-free part acting as cathode (Figure 25). Under specific corrosion environments, the stressed part undergoes corrosion, initiating the crack. In the presence of continuously acting stress and corrosion medium, the crack propagates through the metal. Cracking of brass and caustic embrittlement of steel boilers are two examples of stress corrosion.

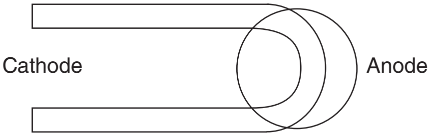


Figure 25 Stress corrosion in metal.

- **Seasonal cracking:** This type of corrosion was first observed during the British rule in India during the monsoon season. Due to diminished military activity during this season, brass cartridges were stored for later usage. After some time, it was found that cracks were developed on the surface of these cartridges. The seasonal cracking occurs due to the action of (a) susceptible agent like copper and its alloys, (b) attacking agent like ammonia and (c) tensile stress (residual).
- **Caustic embrittlement of steel boilers:** Mild steel boilers undergo corrosion at the stressed portion when the operating pressures are between 10 atm and 20 atm. Fine cracks may develop at the stressed portion of the boiler. Boiler water containing alkaline impurities pass into these cracks by capillary action. This water evaporates and leaves behind caustic soda in the cracks, whose concentration increase to 10%. Thus, a galvanic cell is set up between the iron under stress and the iron in the main body. The cell can be represented as follows

$$\underset{\text{(under stress)}}{\text{Iron}} \left| \underset{\text{(in the cracks)}}{\text{Conc.NaOH}} \right| \underset{\text{(in boiling water)}}{\text{dil.NaOH}} \left| \underset{\text{(main body)}}{\text{Iron}} \right.$$

Iron under stress acts as the anode and gets corroded resulting in boiler failure. The boiler water contains Na_2CO_3, which is hydrolyzed at high temperature to give NaOH.

$$Na_2CO_3 + H_2O \xrightarrow{\Delta} 2NaOH + CO_2$$

The NaOH formed flows into hair-thin cracks and crevices. There it reacts with iron and forms Na_2FeO_2 (sodium ferroate) which decomposes to give Fe_3O_4 and NaOH.

$$2NaOH + Fe \rightarrow Na_2FeO_2 + H_2$$
$$3Na_2FeO_2 + 4H_2O \rightarrow Fe_3O_4 + 4H_2 + 6NaOH$$

NaOH thus formed, further reacts with iron to cause corrosion. This is called caustic embrittlement.

Preventive measures

- Applying protective coatings.
- Using corrosion inhibitors.
- Performing stress-relief heat treatments.
- Reducing the overall stress level and designing out stress concentrations.
- Adding Na_2SO_4 to boiler water in addition to tannin and lignin to boiler water to prevent caustic cracking.

2. **Intergranular corrosion:** Generally observed in alloys, this corrosion involves an attack on the grain boundaries of a metal or alloy, where the formation of a corrosion product takes place. This corrosion is not observed externally, and leads to sudden unanticipated failure of the material. For instance, when stainless steel (18% Cr, 8% Ni) containing more than 0.1% carbon is heated to high temperature and cooled slowly or held at 650°C for a short interval of time, a rapid reaction occurs between carbon and chromium. Chromium carbide, thus formed, precipitates at the grain boundaries and results in the formation of galvanic cells (Figure 26).

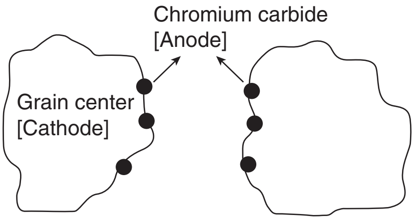


Figure 26 Intergranular corrosion in stainless steel.

Chromium-rich grain centers act as the cathode, while the grain boundaries act as anode and undergo corrosion. This type of corrosion is also called grain-boundary corrosion.

Preventive measures

- Selecting an alloy type resistant to intergranular corrosion.
- Avoiding heat treatments or service exposure that make the material susceptible. Normally, this occurs with austenitic stainless steels when they are held for sometime in the sensitizing temperature range of 470–915°C.
- Applying protective coatings.

3. **Microbiological corrosion:** This corrosion involves degradation of materials by bacteria, moulds and fungi or their byproducts. Some types of bacteria consume oxygen and cause differential aeration type of system, which results in corrosion. The corrosion occurs at the zones poor in oxygen concentration. For example, the bacillus, algae diatoms. This type of corrosion can occur by a range of actions such as:
   - Attack of the metal or protective coating by acid byproducts, sulphur, hydrogen sulphide or ammonia.
   - Direct interaction between the microbes and metal that sustains attack.

   For example, corrosion of steel pipelines in waterlogged neutral ground containing little oxygen is often much more severe than might be expected. Cast iron pipes of 6 mm wall may perforate in less than 5 years. *Sulphate-reducing bacteria* such as *Desulphovibrio* which flourish in oxygen-free conditions assist the corrosion of iron apparently by consuming hydrogen produced in the cathodic reaction, thus enhancing the rate of the cathodic reaction.

$$H^+ + e^- \rightarrow H$$

The bacteria make use of H^+ to reduce sulphate SO_4^{2-} concentration. The overall corrosion cell reaction is as follows:

$$8H^+ + 8e^- \rightarrow 8H^+$$

$$SO_4^{2-} + 8H^+ \rightarrow S^{2-} + 4H_2O$$

The corrosion product FeS is formed as a result of the above reactions.

Preventive measures

- Selecting resistant materials.
- Ensuring frequent cleaning.
- Controlling chemistry of surrounding media and removal of nutrients.
- Using of biocides.
- Applying cathodic protection.

4. **Soil corrosion:** Underground pipes, cables, tank bottoms, etc., get corroded due to moisture, pH of soil, ionic species like chlorides and micro-organisms like bacteria. It is further enhanced by differential aeration of various parts of the soil.
5. **Erosion corrosion:** Due to mechanical wear and tear, there is relative motion of the corrosive liquid over the metal surface. This motion increases the rate of corrosion on the surface of a metal and is called erosion corrosion. It is most common in copper tubes.

Concept Check

- What do you mean by corrosion?
- Give the chemical composition of rust.
- What are the important causes of corrosion?
- What are the effects of corrosion?
- What is meant by dry corrosion?
- Explain briefly theory of dry corrosion.
- What do you mean by wet corrosion?
- Write a note on electrochemical theory of corrosion.
- Distinguish between dry and wet corrosion.
- Explain differential metal corrosion.
- Iron corrodes in contact with copper, but not with zinc. Justify.
- How do you prevent differential metal corrosion or galvanic corrosion?
- Write important preventive measures for galvanic corrosion.
- What do you mean by waterline corrosion?
- Explain the mechanism of pitting corrosion.
- Write a note on crevice corrosion.
- Explain caustic embrittlement in boilers.
- Write a note on intergranular corrosion.
- Explain microbiological corrosion.
- Write important preventive measures for the following types of corrosion: (a) stress corrosion and (b) intergranular corrosion.
- Explain very briefly soil corrosion and erosion corrosion.

Key Terms

Single electrode potential
Standard electrode potential
Electrochemical cells
Electromotive force (EMF)
Salt bridge
Electrochemical series
Equilibrium constant
Nernst equation
Reference electrodes
Standard (normal) hydrogen electrode
Calomel electrode
Primary and secondary cells
Batteries
Dry cell
Lead–acid battery
Alkaline dry cell
Nickel–cadmium cell
Fuel cells
Dry corrosion
Wet corrosion
Electrochemical theory
Differential aeration cell

Objective-Type Questions

Multiple-Choice Questions

1. The standard electrode potential of hydrogen electrode is
   a. 1 V
   b. 10 V
   c. 100 V
   d. 0 V
2. The cell in which electrical energy is converted into chemical energy is called
   a. galvanic cell.
   b. Daniell cell.
   c. electrolytic cell.
   d. electrochemical cell.
3. Which of the following cell converts chemical energy of H_2 gas into electrical energy?
   a. Fuel cell
   b. Daniell cell
   c. Electrolytic cell
   d. Storage cell
4. The relation between ΔG^o and $E^o$is given by
   a. $\Delta G^o = nFE^o$
   b. $\Delta G^o = -nFE^o$
   c. $\Delta G^o = E^o/nF$
   d. $\Delta G^o = RT/nE^o$
5. Among Mg, Al, Zn and Fe, which will displace all the other three from their solutions?
   a. Al
   b. Zn
   c. Mg
   d. Fe
6. In a galvanic cell $E^o_{Cu^{2+}/Cu} = 0.34\,V$ and $E^o_{Zn^{2+}/Zn} = -0.76\,V$. What is E^o_{cell}?
   a. −0.42 V
   b. 0.42 V
   c. −1.10 V
   d. 1.10 V
7. Waterline corrosion in steel tank is an example of
   a. stress corrosion.
   b. differential aeration corrosion.
   c. pitting corrosion.
   d. differential metal corrosion.

Fill in the Blanks

1. In a Daniell cell, the potential difference causes electrons to migrate from ________ through external circuit to ________.
2. In electrochemical series, tendency to gain electron ________ from top to bottom.
3. The EMF of a cell consisting of calomel electrode and standard hydrogen electrode is equal to the EMF of ________ electrode.
4. In the cell represented by $Cd|Cd^{2+} \| Cu^{2+}|Cu$, oxidation occurs at the ________ electrode.
5. The Nernst equation relates ________ to the concentration of reactants and products in half-cells.
6. When the ratio of anodic to cathodic area increases, the rate of corrosion ________.

Review Questions

Short-Answer Questions

1. Explain the origin of single electrode potential.
2. What is standard electrode potential?

3. What is EMF of a cell? How is it determined?
4. What is a galvanic cell? Distinguish between a half-cell and galvanic cell.
5. What is a salt bridge? Why is it used in the construction of a Daniell cell?
6. With the example of Daniell cell, write the following:
   a. reactions occurring at the electrodes
   b. electrical charges at the electrodes.
7. What are electrochemical cells? Distinguish primary cells from secondary cells with examples.
8. Why is electrode potential of zinc assigned a negative value and that of copper assigned a positive value?
9. Why is calomel electrode called a secondary reference electrode?
10. Write the electrode reactions and calculate the EMF the following cell at 298 K given $E^{\mathrm{o}}_{\mathrm{cell}} = 1.3\,\mathrm{V}$.

$$\mathrm{Cu(s)|Cu^{2+}(0.01\,M)||Ag^{+}(0.01\,M)|Ag(s)}$$

11. Distinguish between electrolytic cells and electrochemical cells.
12. A cell consist of following electrodes: (a) copper rod dipped in copper nitrate solution (1M) and (b) silver rod dipped in silver nitrate solution (1 M). Give the following:
    a. cell notation to represent the cell;
    b. half-cell and net cell reaction;
13. Write down the reaction taking place at the separate electrodes in the complete reversible cell given by:

$$\mathrm{Pt, H_2(g)|HCl(aq)||KCl(aq)||AgCl(s)|Ag}$$

14. How does electrochemical series predict the feasibility of a reaction?
15. Explain why:
    a. Nickel spatula cannot be used to stir copper sulphate solution.
    b. Blue color of copper sulphate fades when electrolyzed using platinum electrode.
16. Write the Nernst equation for the following electrode reaction, giving significance of terms:

$$\mathrm{M^{n+}(aq)} + ne^{-} \rightarrow \mathrm{M(s)}$$

17. Write the cell reaction, if the Nernst equation is given by

$$E_{\mathrm{cell}} = E^{\mathrm{o}}_{\mathrm{cell}} - \frac{RT}{2F}\ln\frac{[\mathrm{Pb^{2+}}]}{[\mathrm{H^{+}}]^2}$$

18. Write the Nernst equation for the following cell:

$$\mathrm{Zn\,|\,Zn^{2+}(0.01\,M)\,||\,H^{+}(0.1\,M)\,|\,H_2, Pt}$$

19. Give reasons:
    a. EMF of a cell is always positive.
    b. Reactivity of metal varies inversely with its electrode potential.
20. Can we store $CuSO_4$ solution in znic vessel? Justify your answer. Given

$$E^{\mathrm{o}}_{\mathrm{Cu^{2+}/Cu}} = 0.34\ \mathrm{V} \qquad E^{\mathrm{o}}_{\mathrm{Zn^{2+}/Zn}} = -0.76\ \mathrm{V}$$

21. How is the thermodynamic parameter ΔG related to the electrode potential E?
22. Will zinc (solid) displace Al^{3+}(aq) from a solution? Given $E^{\mathrm{o}}_{\mathrm{Zn^{2+}/Zn}} = -0.76$ V and $E^{\mathrm{o}}_{\mathrm{Al^{3+}/Al}} = -1.66$ V.
23. Given the standard reduction potential of Mg^{2+}/Mg is −2.37 V and Al^{3+}/Al is – 1.066 V. Which one is the strongest reducing agent?
24. Will the following reaction occur in a voltaic cell? Justify your answer.

$$\mathrm{Sn(s) + Fe^{2+}(aq) \rightarrow Sn^{2+} + Fe(s)}$$

Given $E^{\mathrm{o}}_{\mathrm{Fe^{2+}/Fe}} = -0.44$ V; $E^{\mathrm{o}}_{\mathrm{Sn^{2+}/Sn}} = -0.14$ V

25. E^{o} values for Mg^{2+}/Mg = −2.37 V and for Ag^{+}/Ag = 0.80 V. Which is a better oxidizing agent and why?

26. Which is the stronger oxidizing agent between Ni^{2+} and Cu^{2+}? Given: $E^o_{Ni^{2+}/Ni} = -0.25$ V and $E^o_{Cu^{2+}/Cu} = +0.337$ V.
27. Why is quinhydrone electrode not suitable for measurement of pH of alkaline solution?
28. Write down the cell reactions of lead-acid storage cell during charging and discharging process.
29. What are the special properties of lithium that make it advantageous to use as an electrode material?
30. Write the electrode reactions that occur in the Li–MnO_2 cell.
31. Why does dry cell become dead after sometime even if it has not been used?
32. Give example of an alkaline storage battery, along with half-cell and net cell reactions.
33. A lead storage cell can act both as galvanic cell and electrolytic cell. Explain.
34. Explain the following:
    a. The EMF of a lead storage battery is dependent on concentration of sulphuric acid.
    b. In primary alkaline cells, the electrolyte KOH is invariant.
35. Give the half-cell and net cell reactions in the following batteries:
    a. nickel–metal hydride battery;
    b. lithium–manganese dioxide cell.
36. What is a fuel cell? How does a fuel cell differ from a conventional cell?
37. How are fuel cells classified on the basis of: (a) temperature range and (b) type of electrolyte?
38. Mention the reactions involved in a H_2–O_2 fuel cell.
39. Explain the working of methanol–oxygen cell.
40. A pure metal rod half immersed vertically in water starts corroding at the bottom. Give reason.

Long-Answer Questions

1. What are reference electrodes? Mention the limitations of primary reference electrode and advantages of secondary reference electrodes.
2. Write a note on functions of a salt bridge.
3. Derive Nernst equation for the potential of a single electrode from thermodynamic principle.
4. What is a primary reference electrode? Describe the working and construction of hydrogen electrode.
5. Explain the construction and working of the calomel electrode. Mention its advantages.
6. Describe the principle and construction of a glass electrode.
7. Construct the cell for the following cell reactions:

$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu$$

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

$$Fe + SnCl_2 \rightarrow FeCl_2 + Sn$$

8. What is an electrochemical series? Discuss its important applications.
9. Describe the use of standard hydrogen electrode in pH measurement.
10. The overall cell process of an electrochemical cell is

$$AgCl(s) + \tfrac{1}{2}\ H_2\ (g, 1\ atm) \rightarrow Ag\ (s) + HCl\ (aq,\ 0.1\ M).$$

Design and represent the cell schematically and write down the anodic and cathodic reactions at electrodes.

11. Write a note on dry cell.
12. Explain the principle components in a battery and their characteristics.
13. Describe the following with respect to a battery: (a) voltage, (b) current, (c) capacity, (d) energy density and efficiency, (e) life cycle and shelf life.
14. Describe the working of a dry cell using the example of Leclanche cell. How does alkaline battery differ from Leclanche cell?
15. How are batteries classified? What are the factors that affect the EMF of a battery?
16. Describe the construction and working of lead storage battery. Explain the process of recharging in the battery.
17. Explain the construction and working of nickel–cadmium battery along with relevant reactions taking place. What are its advantages and applications?
18. Describe the construction, working, cell reaction and uses of nickel – metal hydride battery.
19. Explain the construction, working and application of lead-acid battery along with reactions involved during discharging and charging.
20. What are fuel cells? How do they differ from conventional galvanic cells? How are they classified?
21. Explain the construction and working of hydrogen–oxygen fuel cells. Give the half-cell reaction and advantages of these cells.
22. Briefly discuss about differential aeration corrosion.

Numerical Problems

1. Construct the cell and calculate the EMF for the reaction:

$$\mathrm{Zn(s)} + \mathrm{Fe}^{2+}(0.005\,\mathrm{M}) \rightleftharpoons$$
$$\mathrm{Zn}^{2+}(0.01\,\mathrm{M}) + \mathrm{Fe(s)}$$

2. For the cell:

$$\mathrm{Fe}|\mathrm{Fe}^{2+}(0.01\,\mathrm{M})||\mathrm{Ag}^{+}(0.1\,\mathrm{M})|\mathrm{Ag}$$

write the cell reaction and calculate the EMF of the cell at 298 K, if standard electrode potentials of Fe and Ag electrodes are −0.44 V and 0.8 V, respectively.

3. Calculate the EMF of the cell from the following data

$$\mathrm{Ni}^{2+}(\mathrm{aq}) + 2e^{-} \rightarrow \mathrm{Ni(s)} \quad E^{\mathrm{o}} = 0.25\ \mathrm{V}$$

$$\mathrm{Cr}^{3+}(\mathrm{aq}) + 3e^{-} \rightarrow \mathrm{Cr(s)} \quad E^{\mathrm{o}} = -0.74\ \mathrm{V}$$

$$[\mathrm{Ni}^{2+}] = 1 \times 10^{-4}\ \mathrm{M} \text{ and } [\mathrm{Cr}^{3+}] = 2 \times 10^{-3}\ \mathrm{M}.$$

4. What voltage will be generated by cell constituted by iron rod immersed in 0.1 M $FeSO_4$ and manganese rod dipped in 0.01 M $MnSO_4$ solution at 25°C. Given $E^{\mathrm{o}}_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = -0.44\ \mathrm{V}$ and $E^{\mathrm{o}}_{\mathrm{Mn}^{2+}/\mathrm{Mn}} = -1.18\ \mathrm{V}$.

5. The EMF of the cell

$$\mathrm{Mg}|\mathrm{Mg}^{2+}(0.1\,\mathrm{M})\,||\,\mathrm{Cu}^{2+}(x\,\mathrm{M})\,|\,\mathrm{Cu}$$

is measured to be 2.78 V at 298 K. Standard electrode potential of magnesium and copper electrodes are −2.371 V and + 0.34 V, respectively. Calculate the concentration of copper ions.

6. Calculate pH of the half-cell: Pt, $H_2 \mid H_2SO_4$. The oxidation electrode potential is +0.3 V.

7. Calculate the equilibrium constant for the following reaction at 298 K

$$\mathrm{Fe}^{2+} + \mathrm{Ce}^{4+} \rightleftharpoons \mathrm{Fe}^{3+} + \mathrm{Ce}^{3+}$$

Given that $E^{\mathrm{o}}_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} = 0.68\ \mathrm{V}$ and $E^{\mathrm{o}}_{\mathrm{Ce}^{4+}/\mathrm{Ce}^{3+}} = 1.44\ \mathrm{V}$.

8. Calculate the EMF of a Cd–Cu cell in which Cd is in contact with 0.002 M $CdSO_4$ and

copper is in contact 0.02 M $CuSO_4$ solution. The standard EMF of the cell is 0.74 V at 298 K.

9. The E^o values of Li^+/Li, Zn^{2+}/Zn, Cu^{2+}/Cu and Ag^+/Ag are –3.0 V, –0.77 V, +0.33 V and +0.80 V, respectively. Which combination of electrodes would you use to construct a cell of highest potential, if ionic concentrations are 1.0 M, 0.1 M, 0.001 M, 0.01 M, respectively.

10. Calculate the equilibrium constant at 25°C for the cell reaction:

$$\mathrm{Ni(s)|Ni^{2+}(aq)||Ag^{+}(aq)|Ag(s)}$$

Given that $E^o_{Ni^{2+}/Ni} = -0.25\,V$ and $E^o_{Ag^+/Ag} =$ 0.80 V.

11. Calculate the potential of Ag–Zn cell at 298 K if the concentration of Ag^+ and Zn^{2+} are 5.2×10^{-6} M and 1.3×10^{-3} M, respectively. E^o of the cell at 298 K is 1.5 V. Calculate the change in free energy ΔG for the reduction of 1 mol of Ag^+ (1 Faraday = 96.5 kJ/Vmol.).

12. Calculate the potential of Daniell cell at 25°C given that the electrode potentials of Cu and Zn are 0.34 V and –0.76 V, respectively.

13. Write the electrode reactions and calculate the EMF of the following cell at 298 K. Given that $E^o_{cell} = 1.3\,V$.

$$\mathrm{Cu(s)\,|\,Cu^{2+}(0.01\,M)\,||\,Ag^{+}(0.01\,M)\,|\,Ag(s)}$$

14. Calculate the standard electrode potential of Cu^{2+}/Cu if its electrode potential at 25°C is 0.296 V when $[Cu^{2+}]$ is 0.015 M.

15. Calculate the EMF of the following cell at 25°C:

$$\mathrm{Ni\,|\,Ni^{2+}(1\,M)\,||\,Pb^{2+}(1\,M)\,|\,Pb}$$

Given that standard electrode potentials of Ni and Pb are –0.24 V and –0.13 V, respectively, at 25°C.

16. Evaluate the equilibrium constant for the formation of tri-iodide ion.

$$I_2 + I^- \rightleftharpoons I_3^-$$

Using the following

$$I_2 + 2e^- \rightarrow 2I^-,\; E^o = 0.6197\,V$$

$$I_3^- + 2e^- \rightarrow 3I^-,\; E^o = 0.5355\,V$$

17. A hydrogen electrode in which the concentration of H^+ is unknown is combined with a normal calomel electrode. The cell has a potential of 0.48 V. Represent the cell, the cell reaction and find out the pH of the solution. (Given $E_{NCE} = 0.28$ V.)

18. A cell consisting of a hydrogen electrode and a saturated calomel electrode has a voltage of 0.4 V when placed in a solution at 298 K. Calculate the pH of the solution. (E for SCE = 0.2415 V).

Answers

Multiple-Choice Questions

1. (d)
2. (c)
3. (a)
4. (b)
5. (c)
6. (d)
7. (b)

Fill in the Blanks

1. zinc, copper
2. increases
3. calomel
4. cadmium
5. electrode potential
6. decreases

Numerical Problems

1. $Zn|Zn^{2+}(0.01)||Fe^{2+}(0.005)|Fe$; 0.231 V
2. At the anode: $Fe \rightarrow Fe^{2+} + 2e^-$

   At the cathode: $Ag^+ + e^- \rightarrow Ag$; 1.24 V

   $$Fe + 2Ag^+ \rightarrow Fe^{2+} + 2Ag$$
3. 0.925 V
4. 0.7695 V
5. 0.234×10^3 M
6. 5.076
7. 7.079×10^{12}
8. 0.7695 V
9. Li^+/Li and Ag^+/Ag
10. 3.388×10^{35}
11. 1.27 V; 122555 J/mol
12. 1.10 V
13. 1.182 V
14. 0.379 V
15. 0.38 V
16. $10^{2.849}$
17. $Pt, H_2(g)\,|\,H^+(\text{unknown conc.})\,||\,NCE$

    At the cathode: $Hg^{2+} + 2e^- \rightarrow Hg$

    At the anode: $H_2 \rightarrow 2H^+ + 2e^-$

    The overall cell reaction:

    $Hg^{2+} + H_2 \rightarrow Hg + 2H^+$
    pH = 3.4
18. 2.7

9 Solid State

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Properties of crystalline and amorphous solids.
- Concept of space lattice and unit cell.
- Different types of unit cells.
- Concept of cubic lattice and calculation of number of atoms, atomic radius and density in cubic lattice.
- Atomic positions and directions in cubic unit cells and Miller indices for crystallographic planes in cubic unit cells.
- Different types of crystal structures.
- Packing of atoms in crystals, efficiency and radius ratio rule.
- Structure of some important ionic solids.
- Defects (imperfections) in solids.

Matter is anything that occupies space and has mass. From a macroscopic view of matter associated with its bulk properties, there are three main phases: gaseous, liquid and solid. A fourth phase, plasma exists at very high temperatures. The gaseous phase of matter is generally transparent and has no definite boundaries other than those imposed by the walls of a confining vessel. Particles of a gas (atoms, molecules or ions) are well separated, have no regular arrangement and move freely at high speeds. Due to the large space in between their atoms (or molecules or ions), gases are highly compressible.

Liquids and solids possess clearly delineated *phase.* Particles of a liquid are close together but have no regular arrangement; they move about and slide past each other. Liquids are relatively incompressible because there is much less free space between the particles in a liquid. Solids are rigid, have a definite shape and the particles are tightly packed, usually arranged in a regular pattern. The particles vibrate about their positions but do not move from place to place. Since the particles of a solid are tightly packed, they are nearly incompressible. Liquids and solids are often referred to as *condensed phases* because the particles in these phases are very closely packed.

9.1 Types of Solids

Solid state of matter is characterized by the rigidity of form and tendency to maintain a definite shape. In solids, the particles are packed in an orderly manner and can be divided into two distinct classes: Crystalline solids and amorphous solids.

Crystalline Solids

Crystalline solids have a well-defined external geometric shape such as a cube, octahedron or tetrahedron and possess the following fundamental properties:

1. They may be composed of atoms, molecules or ions. Crystals made of molecules are held together primarily by covalent bonds and intermolecular forces such as van der Waal forces. Non-molecular crystals could be covalent, ionic or metallic.
2. Their constituent particles have a highly ordered three-dimensional internal arrangement called the **crystal structure**.
3. They have a characteristic external geometrical shape; bound by *planes* or *faces*, with the planes intersecting at particular angles; crystal faces reflect the ordered internal arrangement of atoms.
4. They have sharp melting and boiling points.
5. The magnitude of physical properties such as refractive index, thermal conductivity, etc., shows a variation with the direction in which it is measured. This property is referred to as **anisotropy** and is characteristic of crystalline substances.

Examples of crystalline solids include metals, diamond, graphite and compounds such as NaCl, sugar, $CuSO_4$, $NiSO_4$, etc.

Amorphous Solids

Solids that do not have a definite geometrical shape are known as amorphous solids. These are formed by sudden cooling of a liquid. Their properties are as follows:

1. In these solids, the particles do not have a specific long-range order but are randomly arranged in three dimensions.
2. They do not have sharp melting points but melt over a wide range of temperature.
3. When an amorphous solid is cut with a sharp knife, it results in an irregular cut.
4. These substances exhibit the same values of any physical property in all directions and are said to be **isotropic**.

Examples of amorphous solids include coal, coke, glass, plastic, rubber, etc.

Differences between Amorphous and Crystalline Solids

It is difficult to make a distinction between truly amorphous solids and crystalline solids if the size of the crystal is very small. Even amorphous materials have some short-range order at the atomic length scale due to the nature of chemical bonding. The differences between these solids are listed in Table 1.

Table 1 Difference between amorphous and crystalline solids

Crystalline Solids	*Amorphous Solids*
The arrangement of atoms shows long-range three-dimensional order.	They do not show any long-range ordering.
They posses sharp melting points.	They melt over a wide range of temperature.
They show anisotropy.	They show isotropy.
They are cut along specific crystal planes.	They are cut along random directions and have irregular surfaces.

Concept Check

- What are crystalline solids? How are they different from amorphous solids?
- What are the characteristic features of amorphous solids?

9.2 Space Lattice and Unit Cell

Crystalline solids have an ordered internal arrangement of atoms due to which they *exhibit symmetry*, that is, *the atoms are arranged in a symmetrical fashion in a three-dimensional network*.

A two-dimensional representation of the arrangement of atoms in a crystal is called a **lattice**. It is an orderly array of mathematical points at specific coordinates, with each lattice point having exactly the same environment as any other point representing the same atom or ion. An extension of the array in three dimensions is called a **space lattice** or **crystal lattice**.

A crystal face is commonly developed when it intersects a large number of lattice points. The angles between the crystal faces are determined by the symmetry of the lattice points. By associating a motif (an atom or a group of atoms) to the lattice points of the space lattice, the entire crystal structure can be generated:

$$\text{Crystal structure} = \text{Lattice points} + \text{Motif}$$

A small three-dimensional representative structural subunit of the lattice is called a **unit cell**. This unit cell contains all the necessary points on the lattice that can be translated to repeat itself in an infinite array. In other words, unit cells are the basic building blocks of a crystal and the entire crystal can be built by translation of unit cells identically in the three directions.

The size of the unit cell is defined using **lattice parameters** (also called lattice constants or cell parameters). These are the relative dimensions of the three edges a, b, c of the unit cell along the three axes and the angles between these edges are given by α (angle between b and c); β (angle between a and c) and γ (angle between a and b). The position of the atoms in the unit cell is defined by its coordinates (x, y, z) along the crystallographic axes (Figure 1).

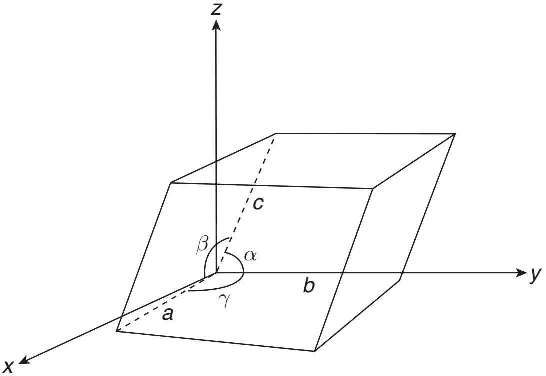
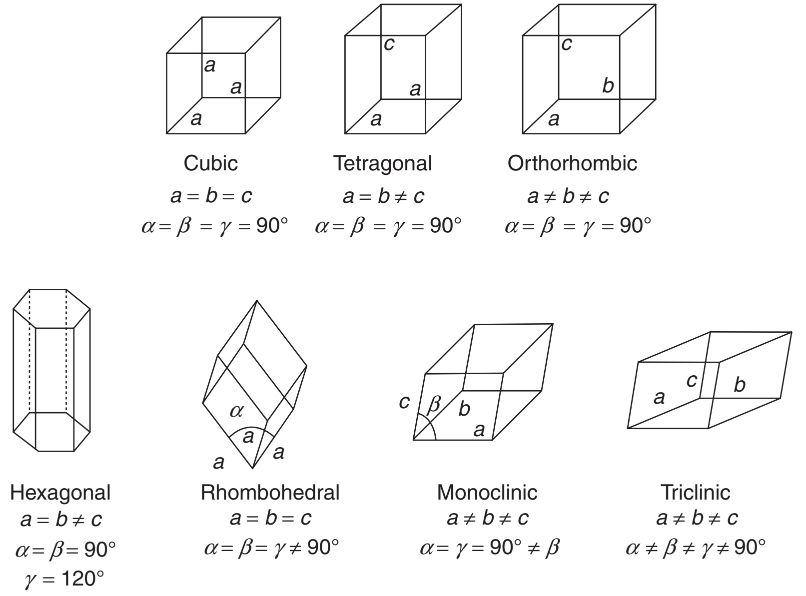


Figure 1 Representation of a unit cell.

9.3 Types of Unit Cell

The shapes of unit cells are restricted by symmetry as well as space considerations, that is, they should be able to arrange themselves in the lattice without gaps and overlaps. Accordingly, there are seven unique and basic unit-cell shapes with varying elements of symmetry in a three-dimensional space. These are called the seven crystal systems, namely, cubic, tetragonal, orthorhombic, hexagonal, rhombohedral, monoclinic and triclinic (Figure 2).



Cubic $a = b = c$ $\alpha = \beta = \gamma = 90°$

Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90°$

Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$

Hexagonal $a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$

Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90°$

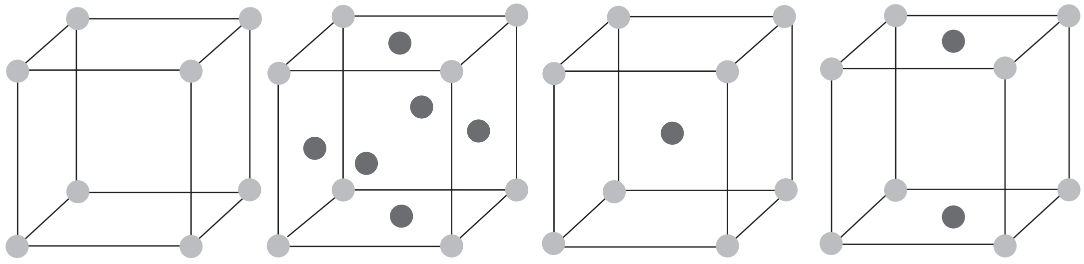
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$

Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$

Figure 2 Types of unit cells.

Each of these seven basic shapes of crystal systems can have any (one or more) of the following types of lattices which are classified as primitive and non-primitive:

1. **Primitive or simple cubic (sc):** In this unit cell, atoms are present only at the corners of the unit cell. The crystal systems with this type of unit cell include cubic, tetragonal, orthorhombic, monoclinic, rhombohedral, hexagonal and triclinic, as represented in Figure 3.
2. **Non-primitive:** In these unit cells, atoms (lattice points) are present not only at the corner of unit cells but also at some other positions. They are further classified as follows:
   - **Body-centered cubic (bcc):** Atoms are present at the corners and one at the center of the unit cell. The crystal systems with this type of unit cell include cubic, tetragonal and orthorhombic.
   - **Face-centered cubic (fcc):** Atoms are present at the corners and at the center of each face of the unit cell. The crystal systems with this type of unit cell include cubic and orthorhombic.
   - **End-centered cubic:** Atoms are present at the center of diagonal joining the nearest neighbors at one set of faces in addition to the atoms at the corner of the unit cell. The crystal systems with this type of unit cell include orthorhombic and monoclinic.



Simple

Face-centered

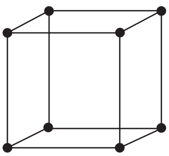
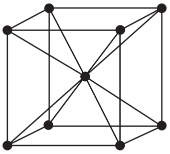
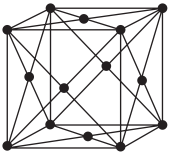
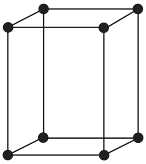
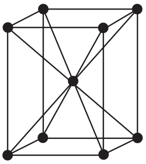
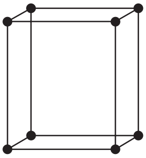
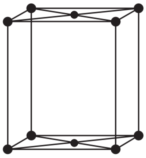
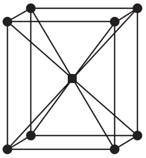
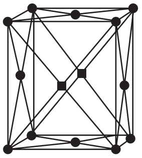
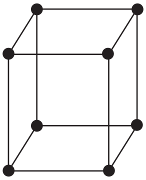
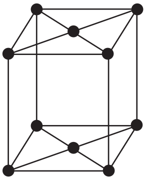
Body-centered

End-centered

Figure 3 Types of lattices in unit cells.

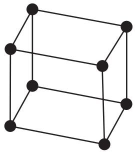
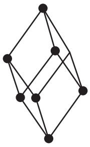
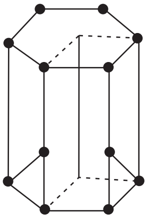
Although each crystal system is expected to have four different unit cells, all of them cannot exist in each case. Symmetry indicates that on combining 7 crystal classes with 4 possible unit cell types, only 14 three-dimensional lattice types (7 primitive or simple, 3 body-centered, 2 face-centered and 2 end-centered) are possible. In 1848, Auguste Bravais demonstrated that, based on geometry, there are, in fact, only 14 possible ways in which similar lattice points can be arranged in regular order in three-dimensional space while maintaining their translational symmetry. For his efforts, crystal lattices are often referred to as **Bravais lattices**. Thus, there are 3 different cubic types, 2 different tetragonal types, 4 different orthorhombic types, 2 different monoclinic types, 1 rhombohedral, 1 hexagonal, and 1 triclinic which constitute the 14 Bravais lattices (Table 2).

Table 2 Crystal classes and Bravais lattices

Crystal Classes	*Bravais Lattices*
Cubic	 Simple  Body-centered  Face-centered
Tetragonal	 Simple  Body-centered
Orthorhombic	 Simple  End-centered  Body-centered  Face-centered
Monoclinic	 Simple  End-centered

(*Continued*)

Table 2 Continued

Crystal Classes	*Bravais Lattices*
Triclinic	 Simple
Rhombohedral	
Hexagonal	

Concept Check

- What is a space lattice?
- What is a unit cell? What are the different types of unit cell?
- What are Bravais lattices?
- What are the different types of cubic lattice?

9.4 Cubic Lattice

From the crystal structure, it is possible to calculate the theoretical density of a compound. Since density is mass per unit volume, it can be calculated by finding the total atomic weight of all atoms in the unit cell and dividing it by the volume of the unit cell. Conversely, if we know the density of the substance and its crystal structure from experiment, then we can calculate the unit cell dimensions and hence the atomic mass of an element. The volume of occupied space contained within the unit cell is calculated by multiplying the number of atoms per unit cell by the volume of a sphere ($V = 4/3\ \pi R^3$).

Therefore, our first step is to know the number of atoms contained within the unit cell. To do this it should be remembered that atoms located at the corners, edges and faces of the unit cell are not fully contained in a single unit cell, so that they only partially occupy the unit cell.

Calculation of Number of Particles per Unit Cell

The number of atoms in a unit cell is calculated by considering the following facts:

1. An atom at the corner of a unit cell is shared by eight unit cells. Hence each atom contributes 1/8 to the unit cell.
2. An atom at the face is a shared by two unit cells, contributing 1/2 to the unit cell.
3. An atom within the body of the unit cell is shared by no other unit cell. Hence, each atom contributes 1 to the unit cell.
4. An atom present on the edge is shared by four unit cells. Hence, each atom on the edge contributes 1/4 to the unit cell.

By applying these rules, we can calculate the number of atoms in the different types of cubic crystal systems:

1. **Simple cubic:**
   Number of atoms in a simple (primitive) cubic unit cell = (8 × 1/8) = 1 atom
2. **Body-centered cubic:**
   Eight atoms at the corners = 8 × 1/8 = 1 atom
   Atoms at the body center = 1 atom
   Number of atoms in a body-centered cubic unit cell = 1 + 1 = 2 atoms
3. **Face-centered cubic:**
   One atom at each corner = (8 × 1/8 each) = 1 atom
   Atoms at each of the six face centers = (6 × 1/2 each) = 3 atoms
   Number of atoms in a face-centered cubic unit cell = 4 atoms

Density Computation

The density of a solid is that of the unit cell. It is obtained by dividing the mass of the atoms in a unit cell by the volume of the unit cell.

$$\text{Mass of the atoms of unit cell} = \text{Number of atoms in a unit cell} \times \text{Mass of an atom } (M_{\text{atom}})$$

$$\text{Mass of one atom} = \frac{\text{Atomic mass } (A)}{\text{Avogadro number } (N_{\text{A}})}$$

Volume of unit cell = $V_c = a^3$ (if it is a cubic unit cell). Thus, the formula for the density is

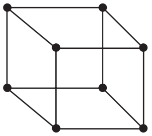
$$\text{Density } (d) = \frac{(\text{Number of atoms/cell}) \times (\text{Atomic mass})}{(\text{Volume of unit cell}) \times (\text{Avagadro's number})}$$

or

$$d = \frac{nA}{V_c \times N_{\text{A}}} = \frac{nA}{a^3 \times N_{\text{A}}} \quad \text{(for a cubic unit cell)}$$

Thus if the crystal structure is known from experiment, then the number of atoms per unit cell and hence the theoretical density of a material can be calculated using the parameters of the crystal system. This is illustrated for the various cubic crystal systems as follows:

1. **Simple cubic:** In simple cubic packing, the atoms touch along the edge of the cube [Figure 4(a)]. Hence the cubic cell edge $a = 2R$, where R is the atomic radius and M_{A} is the atomic mass.

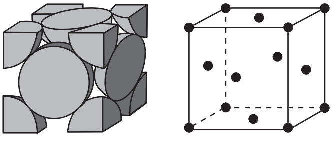


(a)

For simple cubic, $n = 1$, therefore, density is

$$d = 1 \times \frac{M_A}{(2R)^3 N_A} = \frac{M_A}{8N_A R^3}$$

2. **Face-centered cubic:** The hard spheres or ion cores touch one another across a face diagonal [Figure 4(b)]. Therefore, the cube edge length, $a = 2R\sqrt{2}$ [since $(4R)^2 = a^2 + a^2 \Rightarrow (a^2 = 8R^2)$].



(b)

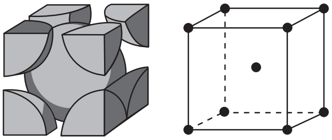
Volume of the unit cell is

$$V = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2}$$

For face-centered cubic, $n = 4$, therefore, density is

$$d = \frac{4M_A/N_A}{16R^3\sqrt{2}} = \frac{M_A\sqrt{2}}{8N_A R^3}$$

3. **Body-centered cubic:** The hard spheres touch one another along cube diagonal [Figure 4(c)]. So, the cube edge length, $a = 4R/\sqrt{3}$ (since diagonal of a cube = 3 times the length of one of its sides). The diagonal of the cube covers $R + 2R + R = 4R$ (as the middle sphere actually touches the two corner spheres).



(c)

Figure 4 Cubic lattice: (a) Simple, (b) face-centered and (c) body-centered.

Volume of the unit cell,

$$V = a^3 = \left(\frac{4R}{\sqrt{3}}\right)^3 = \left(\frac{64}{9}\right)\sqrt{3}R^3$$

For body-centered cubic, $n = 2$, therefore, density is

$$d = \frac{2M_A/N_A}{(64/9)\sqrt{3}R^3} = \frac{9M_A}{32\sqrt{3}N_A R^3}$$

Atomic Positions in Cubic Unit Cells

To locate the position of atoms in cubic unit cells, we use rectangular *x*-, *y*- and *z*-axes, respectively (Figure 5). In crystallography, the positive *x*-axis is usually the direction coming out of the paper, the positive *y*-axis is the direction to the right of the paper and positive *z*-axis is the direction to the top.

These are the atomic positions for eight corner atoms of a bcc unit cell. Central atom has coordinates (1/2, 1/2, 1/2).

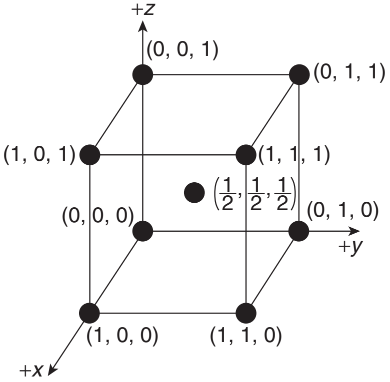
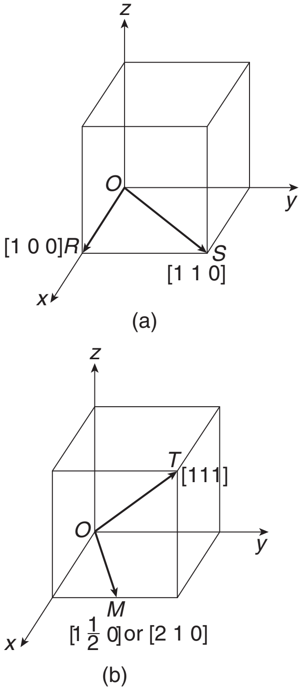


Figure 5 Atomic position in cubic unit cell.

Directions in Cubic Unit Cells

It is always necessary to refer to specific directions in a crystal lattice. This is specially important for metals and alloys that have properties which vary with crystallographic orientations.

For cubic crystals, the crystallographic direction indices are vector components of the direction resolved along each of the coordinate axes and reduced to smallest integers. They are enclosed in the square bracket with no separating commas.



OR: The position coordinates of the direction vector **OR** are (1, 0, 0). So, the direction indices for the direction vector **OR** are [100].

OS: The position coordinates of the direction vector **OS** are (1, 1, 0). So, the direction indices for **OS** are [110].

OT: The position coordinates for the direction vector **OT** are (1, 1, 1). So, the direction indices for **OT** are [111].

OM: The position coordinates of the direction vector **OM** are (1, 1/2, 0). Thus, the direction indices for **OM** are 2(1, 1/2, 0) = [210].

Figure 6 Direction vectors (a) **OR** and **OS** and (b) **OT** and **OM** in cubic unit cells.

Miller Indices for Crystallographic Planes in Cubic Unit Cells

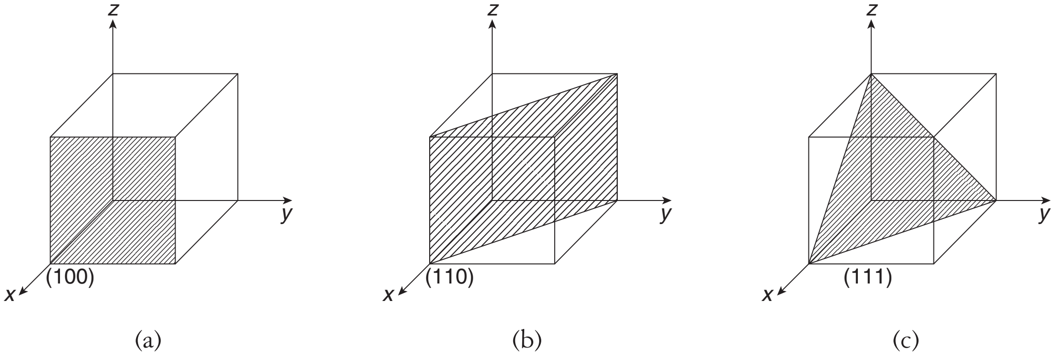
It is necessary to use some convention to specify directions and planes in a crystal. For this purpose, the system introduced by Miller known as **Miller indices** is widely used.

The Miller indices of a crystal plane are defined as the reciprocal of the fractional intercepts, which the plane makes with the crystallographic x-, y- and z-axes of the three non-parallel edges of the cubic unit cell. The procedure for determining the Miller indices is listed as follows:

1. Choose a plane that does not pass through the origin (0, 0, 0).
2. Determine the intercepts of the plane in terms of the crystallographic x-, y- and z-axes for a unit cube. These intercepts may be fractions.
3. Find the reciprocals of these intercepts.
4. Clear the fractions and determine the smallest set of whole numbers which are in the same ratio as the intercepts. These whole numbers are the Miller indices of crystallographic planes and are enclosed in parentheses without using comma. The notation (hkl) is used to indicate Miller indices, where h, k and l are Miller indices of cubic crystal plane for x-, y- and z-axes.

The determination of Miller indices of important crystallographic planes of cubic crystal structures is described as follows:

1. The plane in Figure 7(a) has intercepts 1, ∞, ∞ for x-, y-, z-axes, respectively. We take the reciprocal of the intercepts to obtain Miller indices for this plane (100) or (one-zero-zero plane).
2. The intercepts of the plane in Figure 7(b) are 1, 1, ∞. Since the reciprocals of these are 1, 1, 0, the Miller indices of this plane are (110).
3. The plane in Figure 7(c) has intercepts 1, 1, 1. The reciprocals of these are 1, 1, 1. So, the Miller indices of this crystallographic plane are (111).



(a) (b) (c)

Figure 7 Miller indices of crystallographic planes (a) (100), (b) (110) and (c) (111).

For simple cubic crystals, the lattice vectors are orthogonal and of equal length, denoted by lattice constant a. For these structures, the spacing between adjacent (hkl) lattice planes is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Problem 1

Calculate the density of a bcc crystal, given that length of cube is 4 Å and molar mass is 60.

Solution

Density (d) of the unit cell of a cube crystal is given by

$$d = \frac{nM}{a^3 N_A}$$

Given that $n = 2$ (for bcc) crystal, $M = 60$, $N_A = 6.023 \times 10^{23}$, $a = 4$ Å $= 4 \times 10^{-8}$ cm. So,

$$d = \frac{2 \times 60}{(4 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = \frac{120}{64 \times 10^{-24} \times 6.023 \times 10^{23}}$$

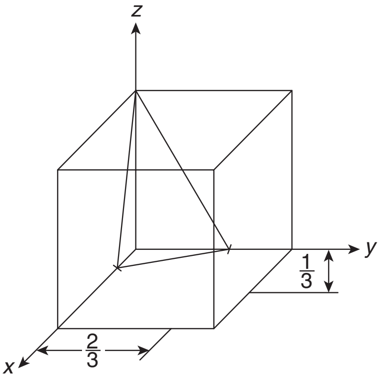
$$= \frac{120}{385.5 \times 10^{-1}} = \frac{1200}{385.5} = 3.11\,\text{g/cm}^3$$

Problem 2

A cubic crystal has intercepts (1/3, 2/3, 1). Find out the Miller indices of the crystal plane and draw the cubic crystal plane.

Solution

This cubic crystal plane has intercepts (1/3, 2/3, 1). The reciprocal of these intercepts are not allowed, these must be multiplied by 2. Thus, the reciprocal of the intercepts become 6, 3, 2 and Miller indices are (632).



Problem 3

Cu has a fcc crystal structure and a unit cell with a lattice constant (a) of 0.361 nm, what is its interplanar spacing d_{220}?

Solution

In cubic crystal structure, the interplanar spacing between two closest parallel planes is designated by d_{hkl}.

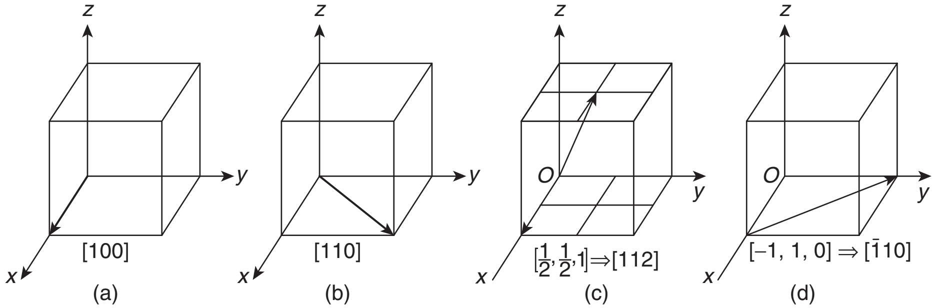
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{0.361}{\sqrt{2^2 + 2^2 + 0^2}} = \frac{0.361}{\sqrt{8}} = 0.127 \text{ nm.}$$

Problem 4

Draw the following direction vectors in cubic unit cells.

(a) {100}, *(b) {110}*, *(c) {112}* and *(d) {$\bar{1}10$}*

Solution



Concept Check

- Calculate the number of particles in simple cubic, body-centered cubic and face-centered cubic unit cells.
- Derive the expression for calculating the density of a crystalline material from the molecular weight and the radius of the atom constituting the crystal in the case of (a) simple cubic, (b) bcc and (c) fcc type of crystal structures.
- Find out the position of atoms in fcc unit cell.
- Draw the [111] direction vector in an atomic site of bcc unit cell and list the atomic positions whose centers are intersected inside the cube by the direction vector.

9.5 Crystal Structure

The crystal structures of many metals, alloys and inorganic compounds can be described geometrically as a packing of equal spheres (atoms), held together by interatomic forces. When the crystal is made of more than one kind of atoms, the positions of one kind of atoms or ions correspond to those of closely packed equal spheres and the other kind of atoms are distributed among the voids in the close-packing. Such structures are generally referred to as close-packed structures.

In order to maximize the bonding in such close-packed crystalline solids, the arrangement or packing of atoms needs to be such that maximum available space is utilized; hence, the crystal has maximum density. In analyzing the efficiency of packing of atoms to meet these criteria, it is assumed that the atoms are hard spheres of identical size. In one dimension, the closest efficient packing is when the spheres just touch each other as shown in Figure 8:

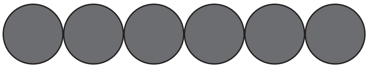
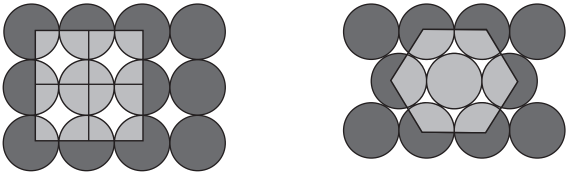


Figure 8 Close packing of sphere in one dimension.

Extending to two dimensions, the arrangement of spheres can be done in two possible ways:

1. **Square close packing:** It is obtained by placing the second row of spheres directly on top of the first row. In such an arrangement, each sphere or atom has four other atoms as its closest neighbors [Figure 9(a)].
2. **Hexagonal close packing:** It is obtained by placing the second row of spheres in the interstices or depressions of the first-row spheres as shown in Figure 9(b). Each sphere or atom has six closest neighbors.

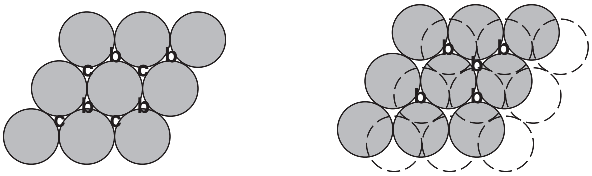


(a) (b)

Figure 9 (a) Square close packing, (b) hexagonal close packing.

The number of closest neighbors that an atom has is called its **coordination number.** Thus it can be seen that in two-dimensional space, hexagonal close packing (hcp) is a more efficient way of packing.

Further extending the packing to three-dimensional space on a hexagonal close-packed two-dimensional stack, the second layer of spheres is placed in the voids created by the first layer as shown in Figures 10(a) and (b). There are two types of triangular voids labeled as b and c. It is to be noted that although there are six voids around each sphere in the first layer, only three of these can be directly covered by placing the spheres of the second layer.



(a) One layer of spheres with two types of voids b and c

(b) Second layer of spheres (dotted circles) placed over b type voids

Figure 10 Hexagonal close packing in three-dimensional space.

Placing the second layer of spheres in any of the two types of voids is identical. However, when it comes to placing the spheres of the third layer, we again have two different possibilities arising:

1. The spheres of the third layer can be placed in the voids of the spheres of second layer such that they are exactly in the same positions as the spheres of first layer as shown in Figure 11. If the spheres of first layer are labeled as A, those of second layer as B, then the third layer is also labeled A. Hence the pattern in this type of packing is ABABAB… and is called **hexagonal close packing** or **hcp**. Each atom in an hcp lattice is surrounded by and touches 12 nearest neighbors, six are in the planar hexagonal array (B layer), and six (three in the A layer above and three in the A layer below) form a trigonal prism around the central atom.

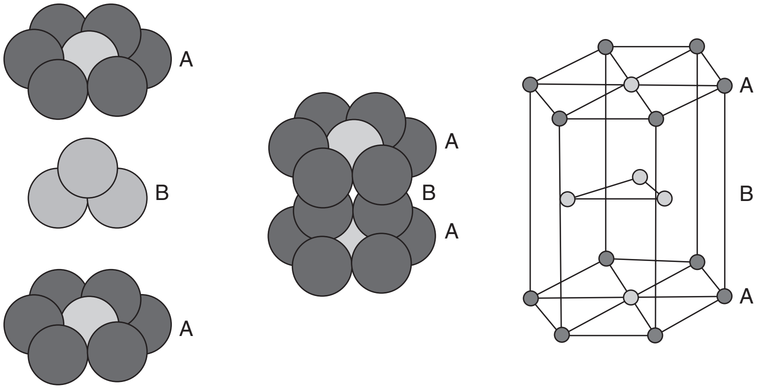


Figure 11 Hexagonal close packing (ABAB…).

2. Alternately, if the atoms in the third layer are placed such that they are on the positions corresponding to the three voids in the A layer which were *not* covered by the atoms in the B layer, then the third layer is different from either A or B and is labeled C. If a fourth layer is placed then it repeats the A layer orientation, and succeeding layers repeat the pattern ABCABCA..., the resulting closest packed structure is called as **cubic close packing** or **ccp** (Figure 12). It is to be noted that only the fcc structure is a close-packed lattice within the cubic system.

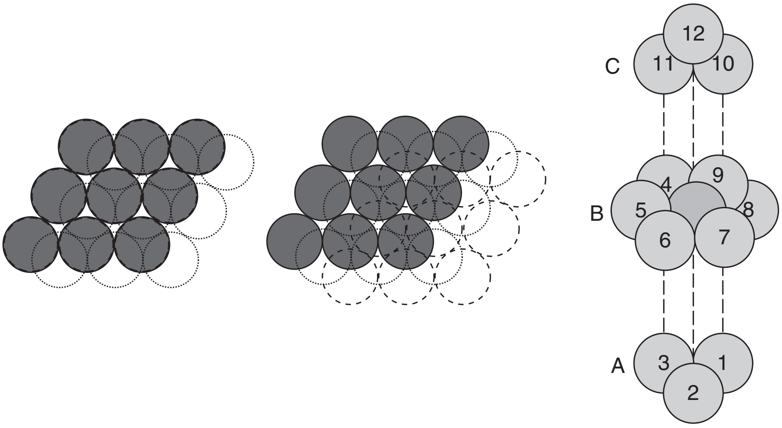


Figure 12 Cubic close packing (ABCABC…)

In both hexagonal and cubic closed packing, an atom/sphere is in contact with 6 others in its own layer; it directly touches three spheres in the layer above and three in the layer below. Thus each sphere has 12 closest neighbors. Thus, in both hcp and ccp each sphere has a coordination number of 12 and this is the maximum coordination number of any sphere for a maximum packing density.

Some examples of hcp are Mg, Zn, Cd and examples of ccp are Na, K, Fe, Cr.

Packing Efficiency

The packing efficiency, *f*, is defined as the fraction of the total volume of the unit cell actually occupied by atoms.

$$\text{Packing efficiency} = \frac{\text{Volume occupied by atoms/spheres}}{\text{Total volume of the unit cell}} \times 100$$

1. **For a simple cubic (sc) structure:** For such an arrangement, the unit cell edge is $a = 2R$, since two spheres just touch each other along the edge as shown in Figure 13:

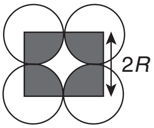


Figure 13 Packing in sc.

Therefore,

$$\text{Packing efficiency} = \frac{1 \times (4/3)\pi R^3}{(2R)^3} \times 100 = \frac{\pi}{6} \times 100 = 52.35\%$$

2. **Face-centered cubic (fcc) arrangement:** For such an arrangement, along each face one sphere touches two others along the diagonal, as shown in Figure 14.

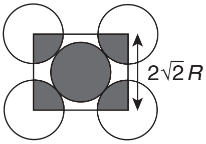


Figure 14 Packing in fcc.

Here, the face diagonal $= R + 2R + R = 4R = \sqrt{a^2 + a^2} = \sqrt{2}a$
where the a is the unit cell edge and R is the radius of the sphere. Therefore,

$$a = 2\sqrt{2}R \quad \text{or} \quad R = a/2\sqrt{2}$$

Also, fcc arrangement in cubic close packing has effectively 4 spheres per unit cell.

Volume of four spheres is $4\times(4/3)\pi R^3$

Volume of the cube is $a^3=(2\sqrt{2}R)^3$

Therefore,

$$\text{Packing efficiency}=\frac{4\times(4/3)\pi R^3\times100}{(2\sqrt{2}\,R)^3}$$

$$=\frac{(16/3)\pi R^3\times100}{16\sqrt{2}R^3}=74\%$$

3. **For body-centered cubic (bcc) structure:** Similarly for a bcc structure, the spheres touch each other along the body diagonal as shown in Figure 15. Hence unit cell edge is

$$a=\frac{4R}{\sqrt{3}}\quad\text{or}\quad R=\frac{\sqrt{3}a}{4}$$

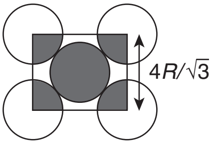


Figure 15 Packing in bcc.

In bcc structure, the total number of atoms per unit cell is 2.
Volume of two spheres is

$$2\times\frac{4}{3}\pi R^3$$

Volume of the cube is

$$a^3=\left(\frac{4}{\sqrt{3}}R\right)^3$$

Therefore,

$$\text{Packing efficiency}=\frac{2\times(4/3)\pi R^3}{(4/\sqrt{3}R)^3}\times100$$

$$=\frac{(8/3)\pi R^3\times100}{64/3\sqrt{3}R^3}=68\%$$

In both type of close packing (hcp and ccp), the efficiency of packing is the amount of available volume occupied by spheres (atoms). Since cubic close packing is similar to face-centered cubic structure, therefore, its packing efficiency is also 74%. Table 3 summarizes packing efficiency and other characteristics of different cubic lattices.

Table 3 Characteristics of different cubic lattices

Characteristic Property	*sc*	*bcc*	*fcc*
Relation between atomic radius (R) and lattice parameter (a)	$a = 2R$	$a = 4R/\sqrt{3}$	$a = 2\sqrt{2}R$
Atoms/cell	1	2	4
Lattice points/cell	1	2	4
Number of nearest neighbors	6	8	12
Packing efficiency	52%	68%	74%

Radius Ratio Rule

In case of close-packed inorganic compounds, the larger atoms or ions (generally the anions) occupy positions corresponding to those of equal spheres as discussed for close-packing earlier, while the smaller atoms (generally the cations) are distributed among the voids. Three-dimensional close-packing of spheres have two kinds of voids and hence two kinds of site for the cation occupancy.

In a crystal structure, when the four spheres touch each other in a tetrahedral arrangement; the space in the center is called a **tetrahedral site** or **void**. The three spheres form the triangular base, the fourth lies at the top and the sphere occupies the tetrahedral void. A tetrahedral void may be represented in a cube as shown in Figure 16.

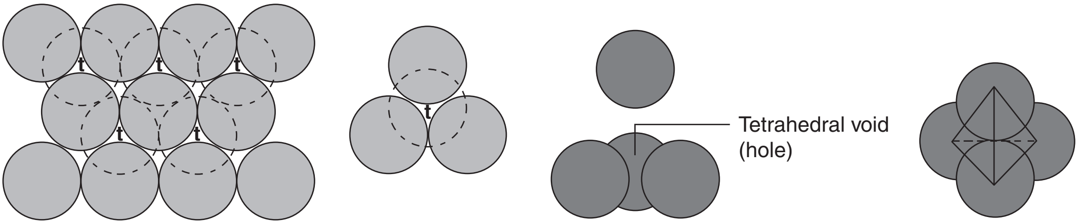


Figure 16 Tetrahedral void.

Similarly, the **octahedral site** or **void** is formed by six spheres touching each other as shown in Figure 17:

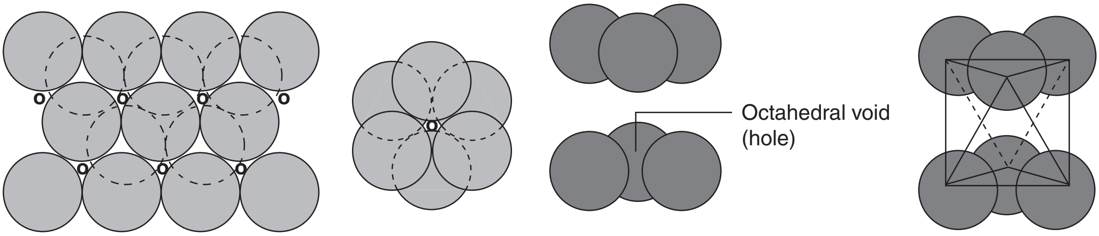


Figure 17 Octahedral void.

Relation between Void Radius and Atomic Radius in Close Packing

Now, in order to determine which kind of atom or ion (cation) would occupy which kind of void, we need to have an idea about the size of these voids in comparison to the size of the spheres. If R denotes the radius of the four identical spheres representing the bigger atom or ion (anion) surrounding a tetrahedral void where the smaller atom could be accommodated, the radius of the sphere r (cation) that would just fit into this void can be obtained as discussed below.

1. **Tetrahedral void:** For the convenience of calculation, if the spheres are assumed to occupy the alternate corners of a cube, then the tetrahedral void would lie on the body diagonal of this cube, just touching the spheres on the opposite corners as shown in Figure 18.

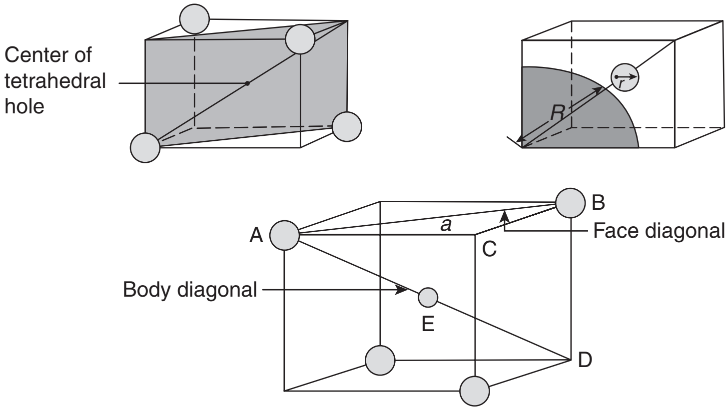


Figure 18 Representation of tetrahedral void.

Let the length of the side of the cube = a
From right-angled triangle ACB, face diagonal

$$\text{AB} = \sqrt{\text{AC}^2 + \text{BC}^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

As spheres A and B are actually touching each other, the face diagonal AB = $2R$. Hence,

$$2R = \sqrt{2}a \quad \text{or} \quad R = \frac{1}{\sqrt{2}}a \tag{9.1}$$

Again from the right-angled triangle ABD, the body diagonal

$$\text{AD} = \sqrt{\text{AB}^2 + \text{BD}^2} = \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$$

But as the smaller sphere in the tetrahedral void touches the bigger spheres along the body diagonal AD = $2(R + r)$, therefore

$$2(R + r) = \sqrt{3}a \Rightarrow R + r = \frac{\sqrt{3}}{2}a \tag{9.2}$$

Dividing Eq. (9.2) by Eq. (9.1), we get

$$\frac{R + r}{R} = \frac{\sqrt{3}a/2}{a/\sqrt{2}} = \frac{\sqrt{3}}{\sqrt{2}}$$

or
$$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = 0.225$$

So, the radius of the tetrahedral void is $r = 0.225\ R$.

2. **Octahedral void:** From the geometry shown in Figure 19:

$$[2(R+r)]^2 (\equiv d^2) = (2R)^2 + (2R)^2$$

or
$$4(R+r)^2 = 8R^2 \Rightarrow (R+r)^2 = (2R)^2 \Rightarrow (R+r) = \sqrt{2}R$$

Therefore,

$$r = \sqrt{2}R - R = R(\sqrt{2} - 1) = R(1.414 - 1)$$

or
$$\frac{r}{R} = 0.414$$

The radius of the octahedral void is $r = 0.414\ R$.

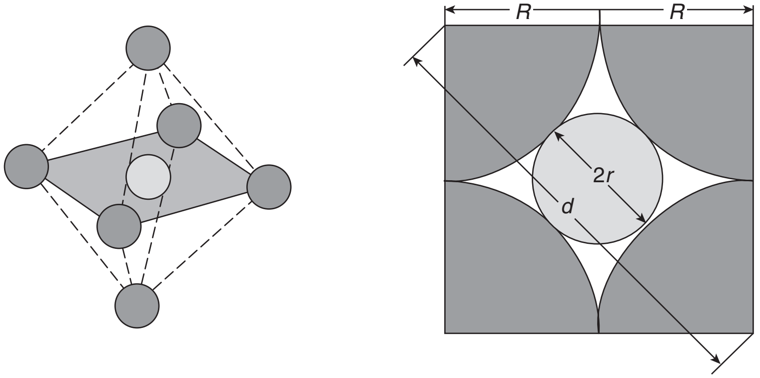


Figure 19 Representation of octahedral void.

Thus it can be seen that when the cation size (r) in relation to the size of the anion (R) increases, the coordination number and hence the structure of the crystal changes. That is, for a smaller size of cation, the closed packed structure would be tetrahedral; and when it increases in size it leads to octahedral arrangement and then to body-centered cubic close packing of the crystal. This fact is represented in the form of radius ratio rules.

The relationship between the radius, the coordination number and the structural arrangement is called the **radius ratio rule**. The larger the size of the cation, the greater is its coordination number. In other words, the greater is the radius ratio, the greater is its coordination number.

$$\text{Radius ratio} = \frac{\text{Radius of cation } (r)}{\text{Radius of anion } (R)}$$

The radius ratio for important crystal systems is summarized in Table 4.

Table 4 Radius ratio and coordination number of important crystal structures

Radius Ratio	*Anions Close Packing*	*Coordination Number*
0.155 to 0.225	Planar triangular	3
0.225 to 0.414	Tetrahedral	4
0.414 to 0.732	Octahedral	6
0.732 to 1.00	Body-centered cubic	8

Problem 5

NH_4Cl crystallizes in a body-centered cubic lattice with edge length of 400 pm. Calculate:
(a) distance between oppositely charged ions in the lattice.
(b) radius of Cl^- ions, if the radius of NH_4^+ is 160 pm.

Solution

For a body-centered cubic lattice:

$$r_{\mathrm{NH_4^+}} + r_{\mathrm{Cl^-}} = \frac{1}{2}\sqrt{3}\,a = \frac{1}{2}\sqrt{3} \times 400 = 346.4\,\mathrm{pm}$$

Given that $r_{\mathrm{NH_4^+}} = 160\,\mathrm{pm},$ so radius of $\mathrm{Cl^-}$ ions is

$$r_{\mathrm{Cl^-}} = 346.4 - 160 = 186.4\,\mathrm{pm}$$

Problem 6

The radius of Cs^+ is 169 pm and that of Cl^- is 181 pm. Predict the structure of CsCl and the coordination number of Cs^+.

Solution

According to radius ratio rule,

$$\frac{r(\mathrm{Cs^+})}{r(\mathrm{Cl^-})} = \frac{169}{181} = 0.933$$

Since range of $r^+/r^- > 0.732$, the coordination number of $\mathrm{Cs^+}$ is 8 and the structure of CsCl is body-centered cubic (bcc).

Problem 7

Sodium chloride has face-centered cubic (fcc) structure. The density of NaCl is 2.163 g/cm^3. Calculate:
(a) edge length of cubic cell;
(b) distance between two adjacent atoms.
Given atomic weight of sodium = 23 and atomic weight of chlorine = 35.5.

Solution

Density (d) of the unit cell of a cubic crystal is given by:

$$d = \frac{nM}{a^3 N_A}$$

where n is the number of atoms per unit cell, M is molecular weight/atomic weight, N_A is Avogadro's number and a is the edge length of cubic cell.

Given that $n = 4$ (for fcc), $M = 58.5$, $N_A = 6.023\times10^{23}$, $d = 2.163$

$$a^3 = \frac{nM}{dN_A}$$

Therefore,

$$a = \left(\frac{n\text{M}}{dN_A}\right)^{1/3} = \left(\frac{4\times58.5}{2.163\times6.023\times10^{23}}\right)^{1/3}$$

$$= (17.972\times10^{-23})^{1/3} = (179.72\times10^{-24})^{1/3}$$

$$= 5.667\times10^{-8}\,\text{cm}$$

For fcc structure, distance between two adjacent atoms is given by:

$$r + r = 2r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2}\times5.667}{4}\times10^{-8} = 2.003\times10^{-8}$$

or $$r = \frac{2.003}{2}\times10^{-8} = 1.001\times10^{-8}\,\text{cm}$$

Concept Check

- What is meant by close packing of atoms/ions? What is the basic assumption in it?
- Explain the two types of close packing of atoms/ions commonly found in crystalline solids.
- Derive the packing efficiency of atoms in simple cubic, bcc and fcc type of unit cells.
- What is radius ratio? What do its values signify?
- Derive the radius ratio rule for tetrahedral and octahedral voids of a close packed crystal structure.

9.6 Structure of Some Ionic Solids

Metals have close packing structures of atoms and hence have high coordination numbers. Ionic solids, however, have lower coordination numbers and can be explained using close packed spheres of ions with the holes in these structures occupied by ions of another kind.

The structures of many ionic solids can be visualized as a close packed arrangement of equivalent negatively charged anions (sometimes the cations) in the fcc or hcp lattices, with the positively charged cations occupying the octahedral and tetrahedral holes in these lattices. We shall look into the crystal structure of some ionic solids in the following subsections.

Structures Based on Face-Centered Cubic Lattices

Rock Salt (or NaCl) Type of Structure

The structure of sodium chloride is based on an fcc arrangement of the larger chloride anions with the sodium cations occupying all the octahedral voids at the body center and edge centers in the fcc lattice. On the other hand, it could also be seen as an fcc packing of sodium ions, with the anions occupying the octahedral voids.

Each of the ions is octahedrally surrounded by six counter ions, and so this structure is called (6,6)-coordination, that is, each Na^+ is surrounded by 6 Cl^- and each Cl^- by 6 Na^+ (Figure 20).

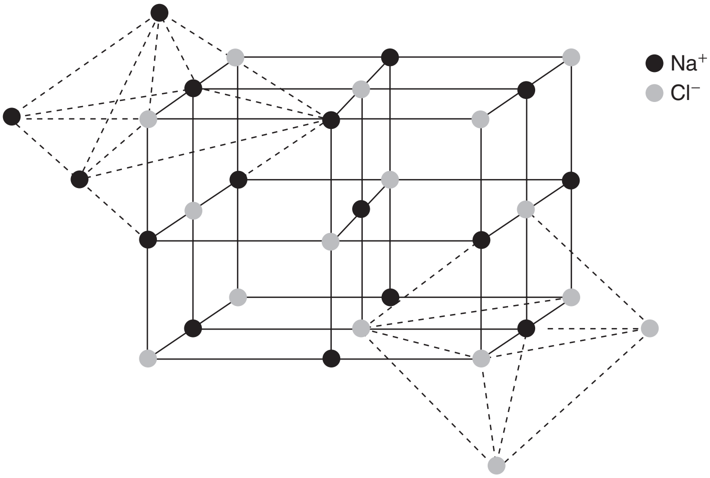


Figure 20 Structure of NaCl.

Number of Cl^- ions in each unit cell:
There are 8 Cl^- at the 8 corners and 6 Cl^- at 6 faces. So, the total number of Cl^- ions is

$$(8\times 1/8)+(6\times 1/2)=1+3=4$$

Number of Na^+ ions in each unit cell:
There are 12 Na^+ at the edge centers and 1 Na^+ at the body center. So, the total number of Na^+ ions is

$$12\times(1/4)+1=3+1=4$$

Total NaCl units in one unit cell: 4.
Other examples of compounds with the NaCl structure include alkali metal halides (except Cs), ammonium halides, silver halides (except silver iodide) and oxides and sulphides of alkaline earth metals (except BeS).

Sphalerite or Zinc Blende (ZnS) Structure

In this structure, there is an fcc packing of sulphide (S^{2-}) anions at the corners and face centers, and the zinc (Zn^{2+}) cations are present in alternate tetrahedral voids. For each atom in the lattice there are two tetrahedral holes; but according to the stoichiometry of the compound (i.e., same number of cations and anions) only half of them have to be occupied.

The Zn^{2+} cations are tetrahedrally surrounded by S^{2-} anions, and each S^{2-} anion is surrounded by eight tetrahedral sites, of which half are occupied by Zn^{2+} ions, and hence the anions are also four-coordinated. The zinc blende structure, therefore, has (4,4)-coordination (Figure 21).

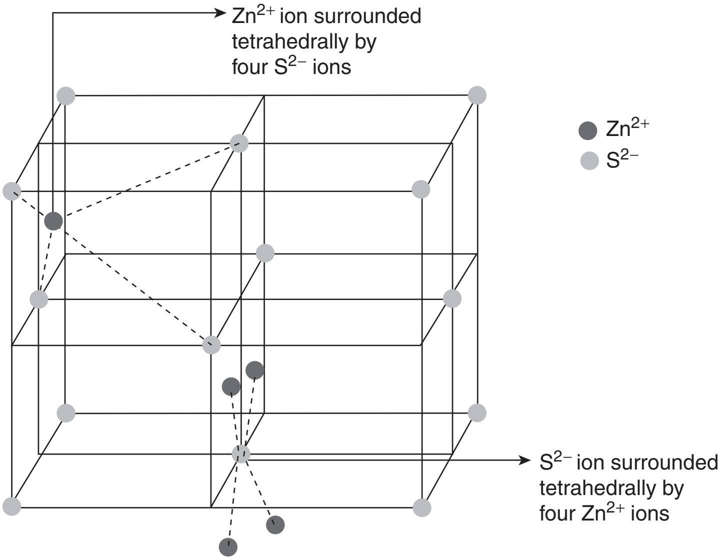


Figure 21 Structure of ZnS.

Number of S^{2-} ions per unit cell:
There are 8 S^{2-} at the corners and 6 S^{2-} ions at the faces. So, the total number of S^{2-} ions per unit cell is

$$8 \times (1/8) + 6 \times (1/2) = 1 + 3 = 4$$

Number of Zn^{2+} ions per unit cell:
Since Zn^{2+} ions occupy only half of the available tetrahedral sites, the number of Zn^{2+} ions per unit cell will be 4.

Total number of ZnS per unit cell: 4.
Other examples of compounds with zinc blende structure include: CuCl, CuBr, CuI, AgI, BeS.

Fluorite Structure (CaF_2)

In this structure, the calcium cations form an fcc lattice, with Ca^{2+} ions at the corners and the face centers, and the fluoride F^- anions occupy all of the tetrahedral voids. For each atom in the fcc array, there are two tetrahedral holes and according to the stoichiometry of the compound both the tetrahedral holes need to be occupied. Thus each F^- anion is tetrahedrally surrounded by 4 Ca^{2+} ions, and each Ca^{2+} cation is surrounded by 8 F^- at tetrahedral sites, all of which are occupied. Hence, the cations are eight-coordinated. So the fluorite structure has (8,4)-coordination (Figure 22). This structure is one of the most common types found in nature.

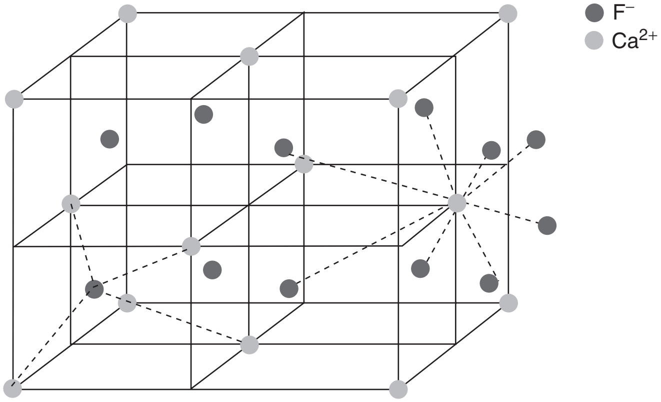


Figure 22 CaF_2 structure.

Other examples of compounds with fluorite structure: BaF_2, $BaCl_2$, SrF_2, $SrCl_2$, etc.

Structures Based on Other Cubic Lattices

1. **Cesium chloride (CsCl) type of structure:** This type of structure is formed when the anion and cation have similar sizes. This is based on a simple cubic lattice of anions with one ion at each of the corners. The cations are located at the center of the anionic cube. The structure can also be considered as a simple cubic array of cations with the anions at the center of the cube. It is an interleaved simple cubic lattice of cations and anions.

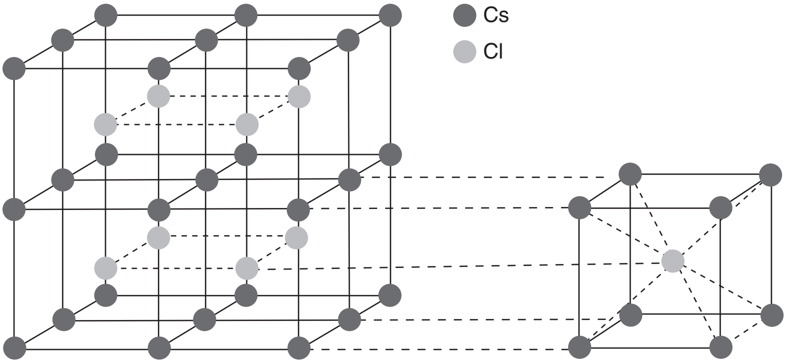


Figure 23 Structure of CsCl.

Each Cs^+ ion is surrounded by 8 Cl^- ions and each Cl^- ion is surrounded by 8 Cs^+ ions. Therefore, the crystal has (8,8)-coordination (Figure 23). With 8 Cl^- ions at corners contributing one Cl^- and one Cs^+ ion in the body center contributing one Cs^+, it has one CsCl per unit cell. Other examples of compounds with cesium chloride type structure include: CsBr, CsI, CsCN, TiCl, TiBr, TiCN, etc.

2. **Perovskite structure:** This structure is adopted by many compounds of the formula ABX_3. In this structure, there is a simple cubic arrangement of B atoms (Ti), with the A atoms (Ca) located at the body center of the cube and the X atoms (O) at the center of the 12 edges of the simple cube. Thus, the central A ion is surrounded by 12 X ions; the B ion by 6 X ions; and the X ion is linearly coordinated by 2 B ions (Figure 24). Examples of compounds with Perovskite structure: $NaNbO_3$, $BaTiO_3$, $CaZrO_3$, $YAlO_3$, $KMgF_3$, etc.

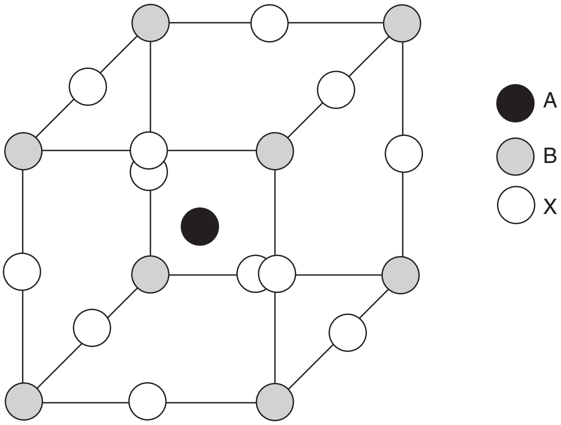


Figure 24 Perovskite (ABX_3) structure.

3. **Antifluorite structure (Na_2O):** The antifluorite structure has the positions of the cations and anions exchanged compared to the fluorite structure, that is, the O^{2-} anions adopt a face-centered cubic arrangement with Na^+ cations in the tetrahedral intersticies.

   The ideal antifluorite would have a cation to anion radius ratio of 0.228. However, the ideal ratio is not observed in the antifluorite structure, the observed ratio is higher than the ideal. Each O^{2-} is surrounded by 8 Na^+ ions. Each Na^+ by 4 O^{2-} ions. Na_2O has (4,8)-coordination (Figure 25). Number of Na_2O per unit cell is 4.

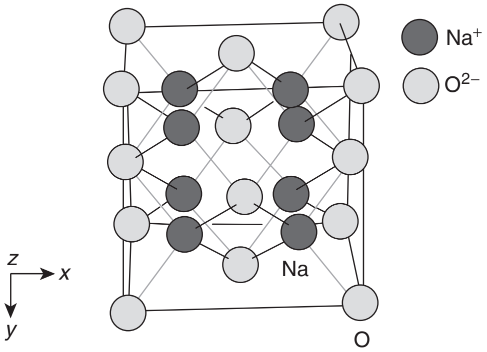


Figure 25 Structure of Na_2O

Antifluorite structure is more commonly found in covalent solids. The alkali metal oxides M_2O (M = Li, Na, K, Rb) crystallize in the antifluorite structure.

Concept Check

- Describe the crystal structure of NaCl and explain how it is different from that of CsCl.
- What is a fluorite structure and how is it different from the antifluorite structure? Give examples of each.

9.7 Imperfection in Solids

Crystals as such are never perfect and in general have some *defect*, which simply refers to a disruption in the periodic order of a crystalline material. These defects occur in crystals because they lower the energy of a crystal and make it more thermodynamically stable. Defects are also known as imperfections in solids.

Types of Imperfections

Defects existing in solid materials are classified on the basis of their geometry as:

1. **Point defects:** In these defects, also known as zero-dimensional point defects, there are points where an atom is missing or is irregularly placed in the lattice structure. These include: Vacancy, interstitial and substitutional atoms.
   - ***Vacancy***: A vacant lattice position in which the atom is missing. It is created when a solid is formed.
   - ***Interstitial***: This defect occurs when an atom occupies a position other than its normal lattice position. The atom in the interstitial may be of the same type as the other atoms of the crystal (self-interstitial) or an impurity atom. Interstitial impurity atoms are much smaller than the atoms in the host matrix and fit into the open space between the host atoms of the lattice structure. One example of interstitial impurity is carbon added to iron to make steel. Carbon atoms (radius of 0.071 nm), fit nicely in the spaces between the larger (0.124 nm) iron atoms.
   - ***Substitutional***: A substitutional impurity is an atom of a different type than the host lattice atom, which replaces one of the bulk atoms in the lattice. Size of these atoms is generally closer (within approximately 15%) to the host atom. Examples of such atoms include the zinc atoms in brass, where zinc atoms (radius of 0.133 nm) replace some of the copper atoms (radius of 0.128 nm).
2. **Line defects:** These defects, also known as single dimensional or linear defects, are groups of atoms in irregular positions. Linear defects are commonly called **dislocations**.
3. **Area defects:** These defects, also known as two-dimensional or surface or planar defects, are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and external surfaces.
4. **Volume defects:** These defects, also known as three-dimensional defects, occur on a much bigger scale than the rest of the crystal defects. For example, voids occurring due to air bubbles become

trapped when a material solidifies. Another type of volume defect occurs when impurity atoms cluster together to form small regions of a different phase.

The number and type of defects in a crystal can be varied and controlled. Defects may be desirable or undesirable and they have a profound effect on material properties. The defects that do not disturb the ratio of cations to anions are called stoichiometric defects. Defects are studied using optical microscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, etc.

In this chapter we confine to the discussion of point defects, which are imperfect point-like regions in the crystal. Their typical size of is about 1–2 atomic diameters. These defects could be due to vacancies and interstitials and include lattice vacancies, self-interstitial atoms, substitution impurity atoms and interstitial impurity atoms.

Due to the presence of both vacancies and interstitial types of defects, there is a change in the coordination and hence an imbalance in the forces around the atoms of defect as compared to other atoms in the solid. This results in distortion of the lattice around the defect (Figure 26).

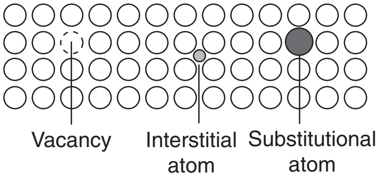


Figure 26 Three types of point defects.

In ionic crystals, point defects satisfy the condition of charge neutrality. There are two possibilities for point defects in ionic solids (Figure 27).

1. **Frenkel defect:** When an ion is displaced from its regular position to an interstitial position, it creates a vacancy; this **vacancy–interstitial pair** is called Frenkel defect. Cations which are generally smaller are easily displaced as compared to anions. For example, in MgO molecule, oxygen ion may leave the lattice and go into interstitial site. These types of defects occur in compounds in which the difference in size of cation and anion is more and coordination number is low, for example, ZnS, AgCl, etc.
2. **Schottky defect:** When a pair of one cation and one anion of equal valency is missing from an ionic crystal, the condition of charge neutrality is still maintained. The pair of vacant sites, thus formed, is called Schottky defect. These **ion–pair vacancies** facilitate atomic diffusion. This type of defect is shown by highly ionic compounds, which have high coordination number and small difference in the sizes of cations and anions. Some ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr and CsCl.

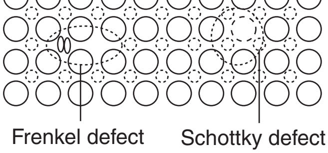


Figure 27 Frenkel and Schottky defects.

Concept Check

- What is meant by imperfections in solids? Why is it important to study these imperfections?
- What are the various types of defects observed in crystalline solids? Explain each in detail.

Key Terms

Crystalline and amorphous solids

Space lattice

Unit cell

Crystal lattice

Lattice parameters

Bravais lattices

Body-, face-, end-centered cubic

Miller indices

Hexagonal and cubic close packing

Packing efficiency

Density of unit cell

Tetrahedral and octahedral voids (holes)

Radius ratio rule

Crystal structures

Defects in solids

Point, line, area defects

Vacancy

Interstitial impurity/atom

Substitutional impurity/atom

Dislocation

Stoichiometric, non-stoichiometric defects

Frenkel and Schottky defects

Objective-Type Questions

Multiple-Choice Questions

1. Three-dimensional array of points in space is called
   a. unit cell.
   b. crystal structure.
   c. hexagonal packing.
   d. crystal lattice.
2. The number of atoms/particles per unit cell for a face-centered cubic lattice is
   a. 1
   b. 2
   c. 3
   d. 4
3. The number of molecules per unit cell in end-centered (monoclinic) lattice with a molecule at each lattice site is
   a. 1
   b. 2
   c. 4
   d. 6
4. The coordination number in a hexagonal close-packed crystal structure is
   a. 12
   b. 8
   c. 6
   d. 4
5. The atomic radius (r) of a body-centered cubic structure is expressed in terms of edge length of cube (a) as
   a. $r = \frac{a}{2}$
   b. $r = \frac{\sqrt{3}\,a}{4}$
   c. $r = \frac{\sqrt{2}\,a}{4}$
   d. $r = \frac{2a}{3}$

6. NaCl has a face-centered cubic close packed structure. What is the coordination number of Na^+ ion?
   - a. 6
   - b. 12
   - c. 8
   - d. 4
7. Which of the following packing types has the lowest packing efficiency?
   - a. cubic close packing
   - b. body-centered cubic
   - c. simple cubic
   - d. hexagonal close packing
8. Which of the following crystals does not have (6,6) coordination?
   - a. NH_4Cl
   - b. ZnS
   - c. MnO
   - d. NH_4Br
9. The coordination number of carbon in diamond (fcc) is
   - a. 4 with 8 carbon atoms in unit cell.
   - b. 4 with 6 carbon atoms in unit cell.
   - c. 6 with 4 carbon atoms in unit cell.
   - d. 4 with 4 carbon atoms in unit cell.
10. Which of the statements is incorrect?
    - a. In hcp and ccp, the sphere is in contact with 6 spheres of its own layer.
    - b. In both hcp and ccp, the sphere has 3 spheres above it and 3 below it.
    - c. In both hcp and ccp, the coordination number is 12.
    - d. Packing efficiency of bcc is more than that of fcc.
11. A compound formed by elements A and B crystallizes in cubic structure, in which atoms of A are at the corners while that of B are at the face center. The formula of the compound is
    - a. AB_3
    - b. AB
    - c. A_3B
    - d. none of the above.
12. The types of Bravais lattices possible for orthorhombic system are
    - a. primitive only.
    - b. primitive and body-centered.
    - c. primitive, body-centered and face-centered.
    - d. primitive, body-centered, face-centered and end-centered.
13. Which of the following expression is correct for a CsCl unit cell with lattice parameter a?
    - a. $r_{Cs^+} + r_{Cl^-} = 2a$
    - b. $r_{Cs^+} + r_{Cl^-} = a/\sqrt{2}$
    - c. $r_{Cs^+} + r_{Cl^-} = (\sqrt{3}/2)a$
    - d. $r_{Cs^+} + r_{Cl^-} = 3a/2$
14. Which of the following is a kind of point defect?
    - a. Frenkel defect
    - b. Schottky defect
    - c. interstitial defect
    - d. All of the above.
15. Which of the following may show Frenkel defect?
    - a. KCl
    - b. NaCl
    - c. AgCl
    - d. CsCl

Fill in the Blanks

1. _________ solids have highly ordered three-dimensional structures with distinct _________ shapes.
2. A solid on heating melts over a range of temperature; it is an example of _________ solid.

3. The phenomenon of solids having different physical properties in different directions is called_________.
4. The 14 basic arrangements of lattices in which the similar points can be arranged in a regular pattern in a three-dimensional space are called _________.
5. The number of possible ways of three-dimensional arrangements of lattice points satisfying translational symmetry is _________.
6. The unit cell with dimensions $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$ is called _________.
7. The number of atoms per unit cell of a face-centered cubic lattice is _________.
8. A body-centered cubic structure has total number of _________ atoms per unit cell.
9. The distance between Na^+ and Cl^- ions in NaCl is 281 pm, therefore the edge length of the unit cell will be _________ pm.
10. The number of nearest neighbors of an atom in their close packing is called _________.
11. In the close packing of atoms, when the arrangement of different layers follows the pattern ABCABC…, then it represents _________ close packing.
12. In fcc packing of atoms, the unit cell edge a is related to atomic radius by _________.
13. Of the three types of cubic close packing of atoms, the packing efficiency is least in _________ and maximum in _________.
14. The coordination number of atoms in hexagonal close packing is _________.
15. When the radius of cation is 0.5 times the radius of the anion, then the anion packing is expected to be _________.
16. The zinc blende structure has _________ coordination.
17. Many compounds of the type ABX_3 adopt _________ type of structure.
18. The lattice defect where the cation moves from the correct lattice site to an interstitial position is called_________.
19. _________ defect causes decrease in density of the crystal.
20. A vacancy–interstitial pair is called_________ defect while a ion-ion pair vacancies is called _________ defect.

Review Questions

Short-Answer Questions

1. Why do solids possess rigid and definite shape?
2. Amorphous solids partly resemble liquids and partly solids. Justify.
3. What are crystalline solids? State the categories of crystalline solids with examples.
4. Define crystal lattice and unit cell.
5. What are different types of unit cells? What is the number of particles per unit cell for each type for a cubic crystal?
6. How are atoms arranged in a body-centered cubic structure?
7. Explain the term Bravais lattice and its relation to crystal structures.
8. What are the Miller indices if the plane intersects the crystal axis at $2a$, b, $2c$?
9. Find out the Miller indices of crystal planes with intercepts $2a$, $3b$, c and $6a$, $3b$, $3c$.
10. Identify the crystal system if $a = 6.5$, $b = 6.5$, $c = 6$, $\alpha = \beta = 90°$ and $\gamma = 120°$.

11. What is radius ratio rule for ionic crystal? What is its significance?
12. Define packing efficiency of ionic crystals. Calculate packing fraction of a simple cubic unit cell.
13. Calculate the packing efficiency of a hcp lattice unit cell.
14. Derive the formula to calculate the density of a cubic crystal, given the edge length of the unit cell.
15. What is meant by stoichiometric defects? Give examples. Are Frenkel and Schottky defects stoichiometric?
16. Impurity defects can alter the mechanical and electrical properties of host materials. Justify the statement with one example each.
17. What are the conditions under which an impurity becomes an interstitial or a substitutional defect?
18. What are the possible types of defects that can occur if a Ca^{2+} ion replaces a Na^+ in the crystal lattice of NaCl?
19. What are the two types of stoichiometric defects?
20. What are two ways by which non-stoichiometric defects due to metal deficiency can occur?
21. What is Frenkel defect?

Long-Answer Questions

1. Distinguish between amorphous and crystalline states of solids. What are the characteristic properties of each type?
2. Discuss the different types of packing in crystals.
3. Discuss Schottky and Frenkel defects. Explain with the help of diagrams.

Numerical Problems

1. The length of a unit cell in body-centered cubic metal crystal is 288.4 pm. Calculate the radius of an atom of the metal.
2. Determine the number of atoms per unit volume if the unit cell contains only one atom at the body center and the lattice constant of the unit cell is 0.6 nm.
3. The radius of lithium ion (Li^+) is 60 pm and that of fluoride ion (F^-) is 136 pm. Calculate the radius ratio and predict the coordination number and crystal structure.
4. The edge length of a face-centered cubic unit cell is 528 pm. If the radius of the cation is 118 pm. Calculate the radius of anion.
5. The edge length of the unit cell of a body-centered cubic metal crystal is 3.5×10^{-12} m. Calculate the radius of an atom of the metal.
6. A compound with fcc crystal structure has a density of 2.163×10^3 kg/m^3. Calculate the edge length of its unit cell.
7. Given the radius of Rb^+ is 1.52 Å and that of Cl^- is 1.81 Å, predict the structure of RbCl and the coordination number of the ions.
8. Calculate the density of chromium which forms body-centered cubic structure, in which the distance between the centers of closest atoms is 255 pm. Given that molar mass of chromium is 52 g/mol.
9. Sodium chloride crystallizes into a face-centered cubic lattice which has edge length of 564 pm. If the density is 2.163×10^3 kg/m^3,

compute the Avogadro's number from the data.

10. The density of KBr is 2.75 g/cm^3 and the edge length of unit cell is 654 pm. What is the number of formula units of KBr present per unit cell and what is the nature of its cubic lattice.

11. An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on its diagonal. If the volume of the unit cell is 24×10^{-24} cm^3 and density of the elements is 7.2 g/cm^3, calculate the number of atoms present in 100 g of the crystal.

12. Given the lattice constant of a fcc type crystal of an element is a = 5.65 Å. Calculate the number of atoms/cm^3 of the element and its theoretical density, if the atomic mass of the element is 145 amu.

13. Silver crystallizes in a cubic close packed structure. The radius of a sliver atom is 1.44 Å. Calculate the density of Ag.

14. A metal with atomic mass 27 has a density of 2.7 g/cm^3 and its unit cell has an edge of 4 Å, what is the nature of the crystal lattice for the metal?

15. Calculate density of a bcc crystal. Side of cube is 4 Å and $M = 60$.

Answers

Multiple-Choice Questions

1. (d)
2. (d)
3. (b)
4. (a)
5. (b)
6. (a)
7. (c)
8. (b)
9. (d)
10. (d)
11. (a)
12. (d)
13. (c)
14. (d)
15. (c)

Fill in the Blanks

1. Crystalline, geometrical
2. amorphous
3. anisotropy
4. Bravais lattice
5. 14
6. tetragonal
7. four
8. two
9. 562
10. coordination number
11. cubic close packing
12. $a2\sqrt{2}R$
13. simple cubic, face-centered cubic
14. twelve
15. octahedral
16. 4,4
17. perovskite
18. Frenkel defect
19. Schottky
20. Frenkel, Schottky

Numerical Problems

1. 124.73 pm
2. 9.26×10^{21} cm^{-3}
3. 0.441; octahedral
4. 255.41 pm
5. 1.52 pm
6. 563.4 pm
7. Body-centered cubic; 8
8. 6.743 g/cm^3
9. 6.03×10^{23} mol^{-1}
10. 4; face-centered cubic
11. 52.08×10^{23} atoms
12. $n = 22.17 \times 10^{21}$ cm^{-3}; $d = 5.34/\text{cm}^3$
13. 10.63 g/cm^3
14. $n = 4$; face-centered cubic
15. 3.11 g/cm^3

10 Polymers

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Polymers and their advantages over traditional materials.
- Some important terms and definitions used to define polymers.
- Classification of polymers based on their origin, structure and properties.
- Functionality and degree of polymerization.
- Different types of polymerization reactions and mechanisms for addition reactions.
- Methods for determining molecular weights of polymers.
- Properties of polymers and their structure–property relationship.
- Glass transition temperature of polymers, factors affecting it and its significance.
- Differences between thermoplastic and thermosetting polymers.
- Composition, properties, methods of manufacture and applications of some commercially important plastics.
- Natural rubber – its processing, properties and compounding techniques.
- Some important synthetic rubbers, their composition, properties, methods of preparation and important uses.
- Fibers, their types and spinning processes.
- Some important synthetic and semi-synthetic fibers.
- Conducting polymers.

Polymers are materials of very high molecular weight that have many applications in our modern society. They usually consist of several structural units bound together by covalent bonds. For example, polyethylene (PE) is a long-chain polymer and is represented as

$$-CH_2-CH_2-CH_2- \text{ or } [-CH_2CH_2-]_n$$

where the structural (or repeat) unit is $-CH_2-CH_2-$ and n represents the chain length of the polymer.

Polymers are obtained through the combination of small molecules called monomers. For example, polyethylene is formed from the monomer ethylene. In order to form polymers, monomers should either have reactive functional groups or a double (or triple) bond whose reaction provides the necessary linkages between repeat units. Polymeric materials find extensive use because of their high strength, and other unique properties such as light weight, high strength-to-weight ratio, processing advantages, corrosion resistance, etc. They are used extensively in food packaging, clothing, home furnishing, transportation, medical devices, information technology, etc.

Natural fibers such as silk, wool and cotton are polymers and have been used for thousands of years. Synthetic polymers such as polyolefins, polyesters, acrylics, nylons, etc., in the past few years have replaced them extensively as clothing and protective materials. It may be added that biological materials such as proteins, deoxyribonucleic acid (DNA) and polysaccharides are also polymers. Many synthetic polymeric materials, known as biomaterials, are increasingly being employed within the human body either as artificial organs, bone cements, dental cements, ligaments, pacemakers or contact lenses because they are inert and hence not rejected by the body. These include natural polymeric materials, which are derived from animals or plants such as cellulose, chitin (or chitosan), dextran, agarose and collagen and synthetic polymeric materials such as polysiloxane, polyurethane, polymethyl methacrylate, polyacrylamide, polyester and polyethylene oxides.

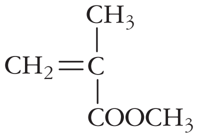
It is being predicted that within a few years, polymers may replace many more conventional materials for various applications. As a result, a large percentage of chemists and engineers are engaged in the work involving polymers, which necessitates the study of polymer science as a separate subject. Further, their behavior as materials is different from that of metals and other materials having low molecular weight.

10.1 Some Important Terms and Definitions

1. **Monomers:** These are simple molecules which combine with each other to form polymers. Monomers are also called "building blocks" of polymers. For example, ethylene, methyl methacrylate, vinyl chloride, etc.

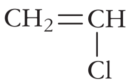
$CH_2{=}CH_2$

Ethylene



$CH_2{=}C(CH_3)(COOCH_3)$

Methyl methacrylate



$CH_2{=}CH(Cl)$

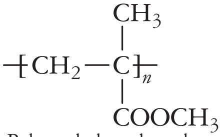
Vinyl chloride

To qualify as a monomer, a molecule should have at least two bonding sites (in the form of double or triple bonds or functional groups such as –OH, –COOH, $-NH_2$, –NCO, etc.).

2. **Polymer:** It is a macromolecule formed by the repeated unit of several simple molecules called monomers. The process of linking the repeating units is called polymerization. The repeating units in a polymer are linked through covalent bonds. For example, polyethylene, polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), etc.

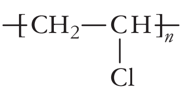
$-\!\!\left[CH_2-CH_2\right]\!\!-_n$

Polyethylene



$-\!\!\left[CH_2-C(CH_3)(COOCH_3)\right]\!\!-_n$

Polymethyl methacrylate



$-\!\!\left[CH_2-CH(Cl)\right]\!\!-_n$

Polyvinyl chloride

3. **Polymerization:** It is the process of conversion of substances having low molecular weight (monomers) into substances having high molecular weight (polymers) with or without the elimination of byproducts such as HCl, H_2O, NH_3, etc. Polymerization reaction usually takes place in the presence of initiators.
4. **Degree of polymerization (DP):** The number of repeating units present in a polymer is called degree of polymerization.

$$\underset{\text{Ethylene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{Polyethylene}}{-\!\!\left[CH_2-CH_2\right]\!\!-_n}$$

Here n is the degree of polymerization. When the value of n is very large, that is, in the range of hundreds or thousands, the polymers are called high polymers. For low values of n, that is, less than 10, the polymers are called oligomers in general; and more specifically as dimers ($n = 2$), trimers ($n = 3$), tetramers ($n = 4$), and so on.

5. **Functionality:** The total number of bonding sites or functional groups present in a monomer molecule is called the functionality of the monomer.
   For example, ethylene (bifunctional), methyl methacrylate (bifunctional), adipic acid (bifunctional), phenol (trifunctional), glycerol (trifunctional), etc.

Concept Check

- Define monomers and polymers.
- What is degree of polymerization?
- What do you understand by functionality of a polymer? Give examples.

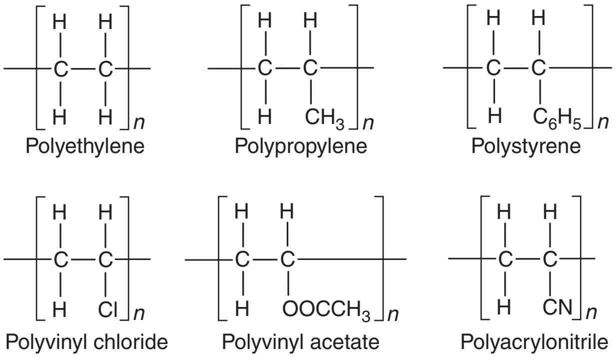
10.2 Classification of Polymers

On the basis of occurrence, thermal behavior, type of polymerization, chemical structures, stereochemistry, mechanical behavior and end-use application, polymers can be classified as follows:

1. **Natural and synthetic polymers:** The polymers obtained from natural sources such as plants and animals are called natural polymers. For example, wood, cellulose, jute, cotton, wool, silk, proteins, natural rubber, etc.

   The polymers synthesized from simple molecules (monomers), are called synthetic polymers. For example, PE, PVC, PMMA, polytetrafluoroethylene (PTFE), polycarbonate (PC), epoxy resin, polyurethane, etc.
2. **Thermoplastic and thermosetting polymers:** The polymers that soften on heating and which can be converted into any shape on cooling are called thermoplastics. The process of heating, reshaping and retaining the shape on cooling can be repeated several times without affecting their properties much. For example, PE, PMMA, PTFE, PC, etc.

   On the other hand, some polymers undergo chemical changes and cross-linking on heating and become permanently hard, rigid and infusible on cooling. These are called thermosetting polymers and they do not soften on reheating; instead they undergo degradation. For example, phenol–formaldehyde (bakelite), urea–formaldehyde, epoxy resin, etc.
3. **Addition and condensation polymers:** The polymers formed by self-addition of several monomers to each other without elimination of byproducts are called addition polymers. For example, PE, PVC, PMMA, etc. as shown in Figure 1.



Polyethylene

Polypropylene

Polystyrene

Polyvinyl chloride

Polyvinyl acetate

Polyacrylonitrile

Figure 1 Examples of addition polymers.

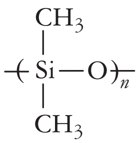
The polymers formed by intermolecular condensation reaction by the functional groups of monomers with continuous elimination of byproducts are called condensation polymers. For example, phenol–formaldehyde resin, polyester, epoxy resin, nylon-6,6, etc.

4. **Linear, branched and cross-linked polymers:** Based on their chemical structure, polymers are classified as linear, branched and cross-linked polymers. For example, bifunctional ethylene monomer polymerizes to yield linear structure of high-density polyethylene (HDPE). All the thermoplastic polymers are essentially linear molecules. Branched chain polymer is formed when a bifunctional monomer is mixed and polymerized with a little amount of trifunctional monomer. Branched polymers contain molecules having a linear backbone with branches arising randomly from it. For example, low-density polyethylene (LDPE), polystyrene, PMMA, etc.

   When the functionality of monomer is 3 and above, cross-linked three-dimensional network of polymer is formed. In fact, whenever a multifunctional monomer is polymerized, the polymer ultimately forms a network polymer. For example, bakelite, urea–formaldehyde, etc.

5. **Organic and inorganic polymers:** A polymer whose backbone chain is essentially made of carbon atoms is termed as an organic polymer. The atoms attached to the side valencies of the backbone carbon atoms are hydrogen, oxygen, nitrogen, etc. Majority of synthetic polymers are organic polymers, for example, PE, PVC, PMMA, etc. On the other hand, the polymers that do not contain a carbon atom in their backbone chain are called inorganic polymers. Some examples include

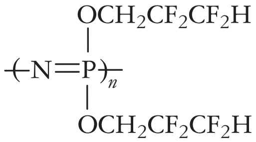
Silicone polymers



$$-\!\left(\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right)_{n}\!-$$

Polyboron nitride polymers $-\!\left(\mathrm{B}{=}\mathrm{N}\right)_{n}\!-$

Polyphosphazene polymers



$$-\!\left(\mathrm{N}{=}\overset{\mathrm{OCH_2CF_2CF_2H}}{\underset{\mathrm{OCH_2CF_2CF_2H}}{\mathrm{P}}}\right)_{n}\!-$$

Polythiazyl polymers $-\!\left(\mathrm{S}{=}\mathrm{N}\right)_{n}\!-$

6. **Atactic, isotactic and syndiotactic polymers:** On the basis of the configuration (stereochemistry) polymers can be classified into three categories, namely, atactic, isotactic and syndiotactic.

   Those polymers, in which arrangement of side groups is random around the main chain are termed as atactic polymers. Polymers in which all the side groups are arranged on the same side of the main chain are known as isotactic polymers. Whereas, those polymers in which the arrangement of side groups is in alternating fashion around the main chain are termed as syndiotactic polymers. For example, polypropylene can exist in the three forms as shown in Figure 2.

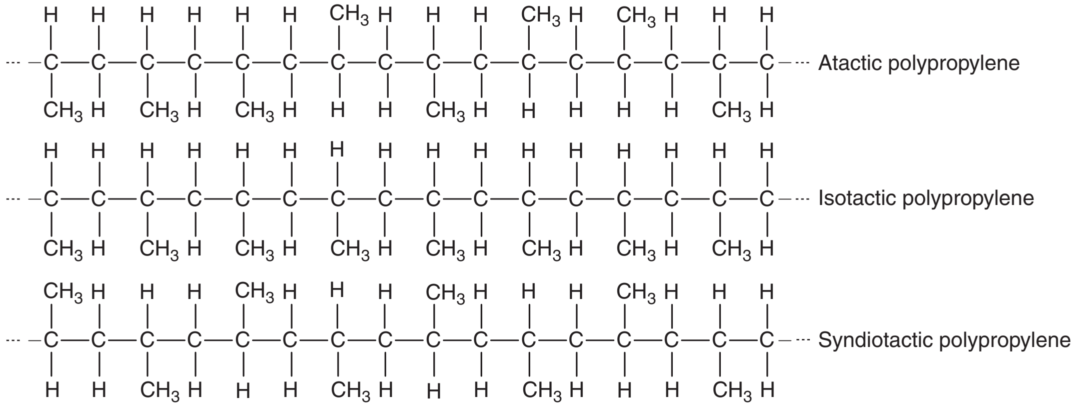


Figure 2 Atactic, isotactic and syndiotactic polymers.

7. **Elastomers, fibers, resins and plastics:** Based on their ultimate structure and end use, polymers are classified as:

   Elastomers: The polymers which undergo very long elongation when pulled apart, and return to their original length on release are called elastomers. These are mainly coiled and long-chain polymers with no intermolecular forces except weak van der Waals forces. For example, natural rubber, Buna-S, butyl rubber, silicone rubber, etc.

   Fibers: These are long, thin and thread-like polymers, whose length is at least 100 times their diameter. They do not undergo stretching and deformation like elastomers, and are linked to each other by hydrogen bonding. For example, natural fibers such as jute, wood, silk, etc. and synthetic fibers such as nylon-6,6 and terylene.

   Resins: These are low molecular weight polymers used as adhesives. They can be in the form of liquid or powder. For example, phenol–formaldehyde, urea–formaldehyde, epoxy resins, etc.

   Plastics: These are polymers, which can be molded into desired shapes by the application of heat and pressure. For example, PE, Plexiglass, PVC, PC, Teflon, etc.
8. **Homopolymers and copolymers:** Polymers formed from the same type of monomers are called homopolymers; for example, polyethylene formed by ethene (ethylene) monomers. If two or more different repeating units (monomers) make up the polymer, it is known as a copolymer, for example, styrene–acrylonitrile (SAN) copolymer, styrene–butadiene (SBR) copolymer, acrylonitrile–butadiene–styrene (ABS) copolymer (Figure 3).

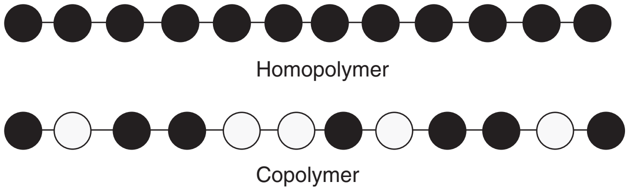


Figure 3 Homopolymer and copolymer.

Concept Check

- How are polymers classified on the basis of their origin and chemical structure?
- Distinguish between thermosetting and thermoplastic polymers.
- Classify polymers on the basis of configuration.
- Distinguish between copolymers and homopolymers.
- How are polymers classified based on their physical structure and end use?

10.3 Types of Polymerization

Addition (Chain) Polymerization

A polymerization reaction in which monomers containing one or more double bonds are linked to each other without the elimination of any byproducts, usually in the presence of free radical initiator, is called addition polymerization. Since in this polymerization the monomers are linked by a chain reaction, it is also called chain polymerization and the polymers formed are called **chain-growth polymers**. For example, the formation of polyethylene

$$\underset{\text{Ethylene}}{n\mathrm{CH_2{=}CH_2}} \xrightarrow{\text{Initiator}} \underset{\text{Polyethylene}}{\left[\mathrm{CH_2{-}CH_2}\right]_n}$$

The main features of addition (chain) polymerization are as follows:

1. Only olefinic or vinyl compounds can undergo addition polymerization.
2. No elimination of byproducts.
3. Double bond provides required bonding sites.
4. The addition of monomers takes place rapidly.
5. Polymerization is brought about by initiators like free radicals.
6. The elemental composition of the polymer is the same as that of monomer.

Condensation (Step) Polymerization

A polymerization reaction in which bifunctional or polyfunctional monomers undergo intermolecular condensation with continuous elimination of byproducts, such as H_2O, HCl, NH_3, etc., is called condensation polymerization. Since the reaction occurs in steps and the polymer chain grows with each step, it is also called step polymerization and the polymers formed are called **step-growth polymers**. The reaction is normally catalyzed by acids or bases. Some examples are as follows:

Formation of nylon-6,6:

$$\underset{\text{Hexamethylenediamine}}{n\mathrm{NH_2{-}(CH_2)_6{-}NH_2}} + \underset{\text{Adipic acid}}{n\mathrm{HOOC{-}(CH_2)_4{-}COOH}} \xrightarrow{\text{Initiator}} \underset{\text{Nylon-6,6}}{\left[\mathrm{NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO}\right]_n} + 2n\mathrm{H_2O}$$

Formation of polyester:

$$\underset{\text{Ethylene glycol}}{n\,\mathrm{OH{-}(CH_2)_2{-}OH}} + \underset{\text{Terephthalic acid}}{n\,\mathrm{HOOC{-}C_6H_4{-}COOH}} \longrightarrow \underset{\text{Polyester (terylene)}}{\mathrm{\left[O{-}(CH_2]_2{-}OOC{-}C_6H_4{-}CO\right]_n}} + 2n\mathrm{H_2O}$$

The main features of condensation polymerization are as follows:

1. The monomers having two or more reactive functional groups can undergo condensation polymerization.
2. There is continuous elimination of byproducts.
3. Polymerization proceeds through intermolecular condensation.
4. Polymerization is catalyzed by acids or alkali.
5. The polymer chain built up is slow and stepwise.
6. The elemental composition of the polymer is different from that of the monomers.

Copolymerization

The polymerization of two or more different monomers resulting in the formation of a polymer containing both monomers linked in one chain is called copolymerization. It can be considered as a type of addition polymerization. The polymers so formed are called copolymers and can have any of the following three structures.

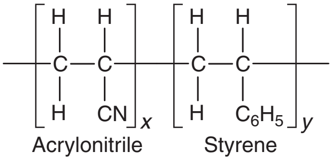
If the various repeating units occur randomly along the chain structure, the polymer is called a **random** copolymer. When repeating units of each kind appear in blocks, it is called a **block** copolymer. **Graft** copolymers are formed when chains of one kind are attached to the backbone of a different polymer.

For example, in case of linear chains synthesized from repeat units A and B, the block, random and graft copolymers can be represented as shown in Table 1:

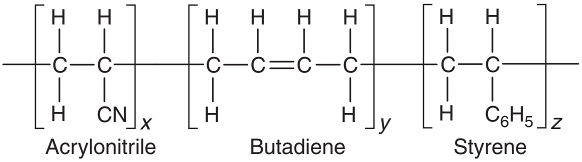
Table 1 Copolymers and their representation

Copolymer	*Representation*
Block copolymer	–A–A–A–A–A–A–B–B–B–B–B–B–
Random copolymer	–A–A–B–A–B–B–A–B–A–A–B–A–
Graft copolymer	$\begin{array}{cccccccc} -\mathrm{A} & -\mathrm{A} & -\mathrm{A} & -\mathrm{A} & -\mathrm{A} & -\mathrm{A} & -\mathrm{A} & -\mathrm{A}- \\ & \vert & & & \vert & & & \\ & \mathrm{B} & & & \mathrm{B} & & & \\ & \vert & & & \vert & & & \\ & \mathrm{B} & & & \mathrm{B} & & & \\ & \vert & & & \vert & & & \\ & \mathrm{B} & & & \mathrm{B} & & & \end{array}$

Examples of copolymers include acrylonitrile–styrene (SAN), ethylene–vinyl acetate (EVA), acrylonitrile–butadiene–styrene (ABS), etc., as shown in Figure 4.



Acrylonitrile–styrene copolymer



Acrylonitrile–butadiene–styrene copolymer

Figure 4 Examples of copolymers.

Concept Check

- What is addition polymerization? Give its characteristic features.
- What is the necessary condition for a monomer to undergo condensation polymerization?
- List the main features of condensation polymerization.
- What are graft and block copolymers? Give examples.
- State the differences between addition and condensation polymerizations.

10.4 Mechanism of Addition Polymerization

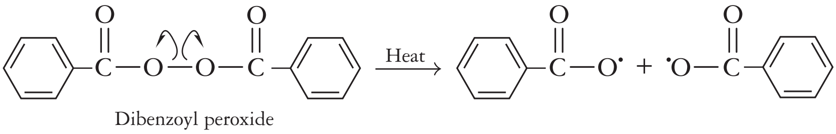
Free Radical Mechanism

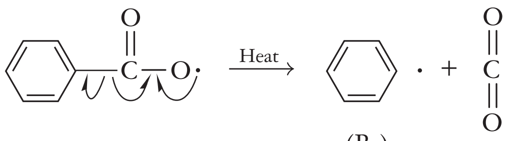
Addition polymerization that takes place through free radical mechanism involves three distinct stages: *initiation*, *propagation* and *termination*.

Initiation

This process involves two reactions.

1. This part involves the production of free radicals by the homolytic dissociation of an initiator, such as dibenzoyl peroxide to yield a pair of radicals. A free radical is an atomic or molecular species having an odd or unpaired electron. They are highly active species.





(R•)

Benzoyl free radical

2. This part of initiation involves the addition of this radical to the first monomer molecule to produce the chain initiating species.

$$\dot{R} + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}\dot{C}H_2$$

Propagation

In propagation, the radical attacks another monomer to produce yet another free radical and the process continues until termination occurs.

$$R{-}CH_2{-}\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2$$

$$\Big\downarrow {\scriptstyle nCH_2 = CH_2}$$

$$R{-}(CH_2{-}CH_2)_n{-}CH_2{-}\dot{C}H_2$$

Termination

At some point, the propagating polymer chain stops growing and terminates. Termination can happen by

1. Coupling or combination of two growing chains

$$R{-}(CH_2{-}CH_2)_n{-}CH_2{-}\dot{C}H_2 + \dot{C}H_2{-}CH_2{-}(CH_2{-}CH_2)_n{-}R$$

$$\Big\downarrow$$

$$R{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}(CH_2)_n{-}R$$

Dead polymer

2. Coupling of growing chain with initiator free radical

$$R{-}(CH_2{-}CH_2)_n{-}CH_2{-}\dot{C}H_2 + \dot{R} \longrightarrow R{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_2{-}R$$

Dead polymer

3. Disproportionation, in which a hydrogen atom of one growing chain is transferred to another growing chain. This results in formation of two dead polymer chains: one having saturated and the other having unsaturated end.

$$\mathrm{R{-}(CH_2{-}CH_2)_n{-}CH_2{-}\dot{C}H_2 + \dot{C}H_2{-}CH_2{-}(CH_2{-}CH_2)_n{-}R}$$

$$\downarrow$$

$$\underset{\text{Saturated dead polymer}}{\mathrm{R{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_3}} \quad + \quad \underset{\text{Unsaturated dead polymer}}{\mathrm{CH_2{=}CH{-}(CH_2{-}CH_2)_n{-}R}}$$

Ionic Polymerization

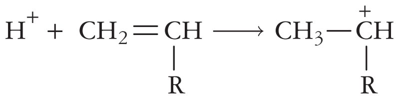
Addition polymerization can also be initiated by ionic species instead of free radicals and this is known as ionic addition polymerization. It can be classified into two types – cationic and anionic, depending on the nature of ionic initiator involved.

Cationic Polymerization

In cationic addition polymerization, the initiator is a cation obtained either from protonic acids (HCl, HNO_3, H_2SO_4) or lewis acids ($AlCl_3$, BF_3, etc.). In case of lewis acid, presence of water is essential as a cocatalyst. Some common examples of cationic polymerization are homopolymerization of isobutylene and copolymerization of isobutylene with 2-methyl propene.

The various steps involved in the mechanism are explained as follows:

1. **Initiation:** The addition of cation to the double bond of the monomer leads to the formation of a carbonium ion (positively charged ionic species with trivalent carbon) and this initiates the polymerization.

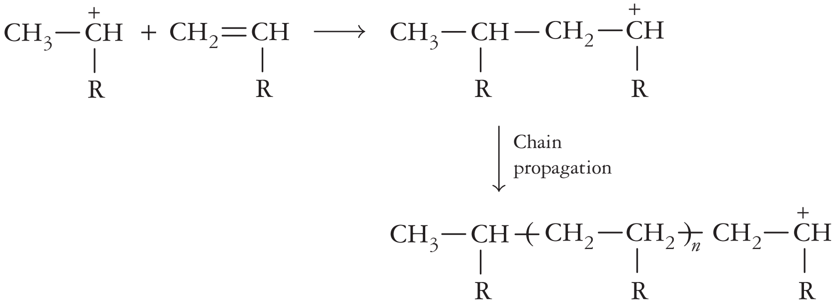


$$\mathrm{H^+ + CH_2{=}\underset{\substack{|\\ R}}{CH} \longrightarrow CH_3{-}\underset{\substack{|\\ R}}{\overset{+}{C}H}}$$

Carbonium ion

   The presence of an electron releasing group facilitates the reaction by stabilizing the carbonium ion formed.

2. **Propagation:** In the next step, the carbonium ion formed adds to the double bond of another monomer, generating a bigger carbonium ion and the chain propagates in a similar manner.

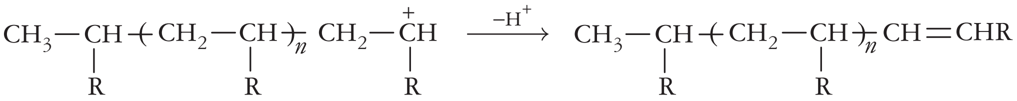


$$\mathrm{CH_3{-}\underset{\substack{|\\ R}}{\overset{+}{C}H} + CH_2{=}\underset{\substack{|\\ R}}{CH} \longrightarrow CH_3{-}\underset{\substack{|\\ R}}{CH}{-}CH_2{-}\underset{\substack{|\\ R}}{\overset{+}{C}H}}$$

$$\Big\downarrow \text{Chain propagation}$$

$$\mathrm{CH_3{-}\underset{\substack{|\\ R}}{CH}{+}\!\!(CH_2{-}\underset{\substack{|\\ R}}{CH_2})_n\, CH_2{-}\underset{\substack{|\\ R}}{\overset{+}{C}H}}$$

3. **Termination:** The chain is terminated by the removal of H^+.

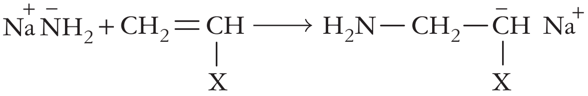


$$\mathrm{CH_3{-}\underset{\substack{|\\ R}}{CH}(CH_2{-}\underset{\substack{|\\ R}}{CH})_n\, CH_2{-}\underset{\substack{|\\ R}}{\overset{+}{C}H} \xrightarrow{-H^+} CH_3{-}\underset{\substack{|\\ R}}{CH}(CH_2{-}\underset{\substack{|\\ R}}{CH})_n\, CH{=}CHR}$$

Anionic Polymerization

Anionic addition polymerization proceeds in the presence of anionic initiators such as alkali metal amides (e.g., sodium or potassium amide) or alkali metal alkyls (e.g., *n*-butyl lithium). Some common examples of anionic polymerization include polymerization of styrene, acrylonitrile and methyl methacrylate. The various steps involved in the mechanism are described as follows:

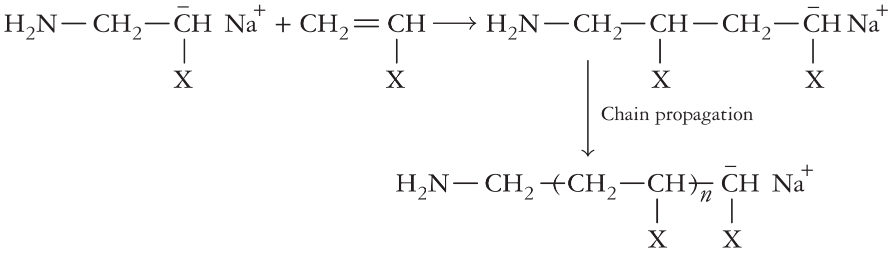
1. **Initiation:** The anionic initiator adds to the electron deficient site of the alkene monomer resulting in the formation of a carbanion (negatively charged species with trivalent carbon) and this initiates the polymerization.



$$\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{N}}\mathrm{H_2} + \mathrm{CH_2}{=}\underset{\mathrm{X}}{\underset{|}{\mathrm{CH}}} \longrightarrow \mathrm{H_2N}-\mathrm{CH_2}-\underset{\mathrm{X}}{\underset{|}{\overset{-}{\mathrm{C}}\mathrm{H}}}\ \mathrm{Na}^{+}$$

   where X is an electron withdrawing group. The presence of an electron withdrawing group facilitates the reaction by stabilizing the carbanion formed.

2. **Propagation:** In the next step, the carbanion formed adds to the double bond of another monomer generating a bigger carbanion ion and the chain propagates in a similar manner.

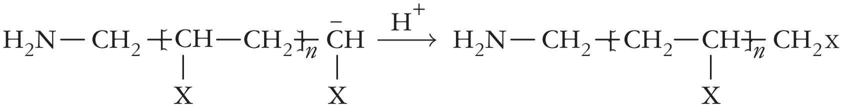


$$\mathrm{H_2N}-\mathrm{CH_2}-\underset{\mathrm{X}}{\underset{|}{\overset{-}{\mathrm{C}}\mathrm{H}}}\ \mathrm{Na}^{+} + \mathrm{CH_2}{=}\underset{\mathrm{X}}{\underset{|}{\mathrm{CH}}} \longrightarrow \mathrm{H_2N}-\mathrm{CH_2}-\underset{\mathrm{X}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{X}}{\underset{|}{\overset{-}{\mathrm{C}}\mathrm{H}}}\,\mathrm{Na}^{+}$$

$$\Big\downarrow \text{Chain propagation}$$

$$\mathrm{H_2N}-\mathrm{CH_2}\left(\mathrm{CH_2}-\underset{\mathrm{X}}{\underset{|}{\mathrm{CH}}}\right)_{n}\underset{\mathrm{X}}{\underset{|}{\overset{-}{\mathrm{C}}\mathrm{H}}}\ \mathrm{Na}^{+}$$

3. **Termination:** The polymeric anionic chain is quite stable and continues to grow until terminated by addition of an acid.

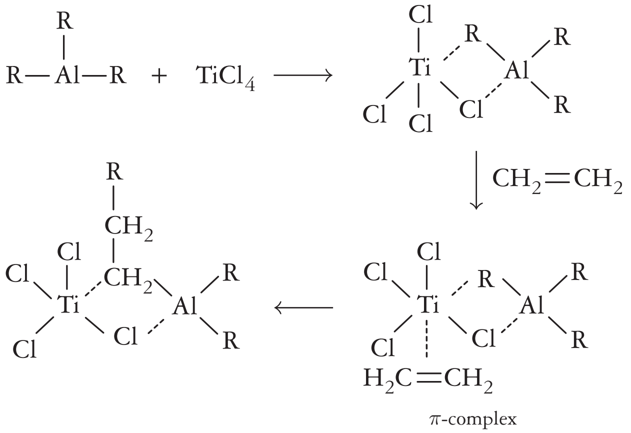


$$\mathrm{H_2N}-\mathrm{CH_2}\left[\underset{\mathrm{X}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}\right]_{n}\underset{\mathrm{X}}{\underset{|}{\overset{-}{\mathrm{C}}\mathrm{H}}} \xrightarrow{\mathrm{H}^{+}} \mathrm{H_2N}-\mathrm{CH_2}\left[\mathrm{CH_2}-\underset{\mathrm{X}}{\underset{|}{\mathrm{CH}}}\right]_{n}\mathrm{CH_2x}$$

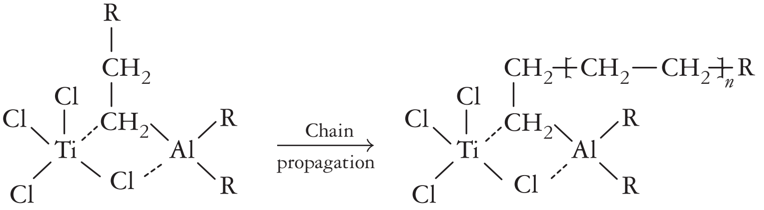
Coordination Polymerization

In coordination addition polymerization, an organometallic active intermediate acts as the initiator. This generally involves the use of Ziegler–Natta catalysts, which is a metal–organic complex of metal ion from Groups 1, 2 and 13 and metal compounds from Groups 1, 2, 13 and 14. For example, a combination of triethylaluminium and titanium tetrachloride. This polymerization results in the formation of stereospecific polymers. The mechanism can be explained as follows.

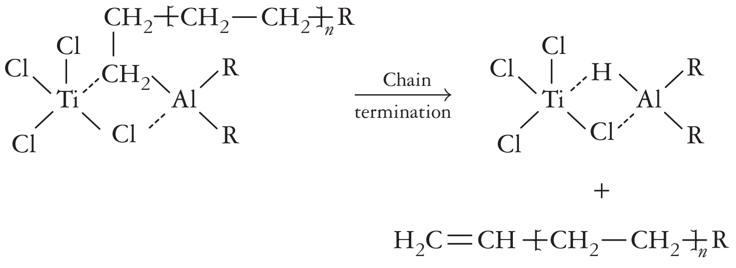
1. **Initiation:** The transition metal serves as the active site. The alkene monomer is held at the active site by formation of a π-complex with the transition metal (titanium). It gets inserted between the metal and the alkyl group *R*. This coordination process results in the stereospecificity of the polymerization.



2. **Propagation:** The migration of alkene monomer between metal and alkyl group initiates the polymerization by facilitating the formation of π-complex with new monomer and the process continues in a similar manner



3. **Termination:** The termination of the chain occurs when the monomer migrates and forms an inactive site, so that polymerization does not proceed further.



Concept Check

- What are the initiators in the free radical polymerization process? Give example.
- Write the reactions involved in different steps of free radical polymerization of ethylene.
- Explain how addition polymerization proceeds through cationic polymerization.
- Discuss the mechanism of anionic addition polymerization.
- Explain the mechanism of coordination addition polymerization using Zeigler-Natta catalyst.

10.5 Molecular Weights of Polymers

Molecular weight is an extremely important variable in the study of polymers because it relates directly to the physical properties of macromolecules. In general, higher the molecular weight, tougher the polymer; however, too high molecular weight will lead to processing difficulties. There are several other reasons why we should measure the molecular weight. The molecular weight and its distribution determines the viscous and elastic properties of the molten polymer.

A variety of methods are available for molecular weight determination, and they are applicable in different ranges of molecular weight. Methods such as end-group analysis and measurement of colligative properties (i.e., freezing point depression, boiling point elevation, osmotic pressure) give the **number average molecular weight** $(\overline{M_n})$. The number average molecular weight is the product of the sample weight and Avogadro's number when divided by the total number of molecules. It is represented as

$$\overline{M_n} = \frac{\sum M_i N_i}{\sum N_i}$$

where N_i is the number of molecules or the number of moles of those molecules having molecular weight M_i.

This technique works well with linear molecules having two reactive end groups that can each be titrated in solution. Consequently, linear condensation polymers made by step-growth polymerization and possessing carboxyl, hydroxyl or amine chain ends are logical candidates for end-group analysis.

Light scattering and ultracentrifugation on the other hand, furnishes the **weight-average molecular weight** $(\overline{M_w})$ and the size of the polymer in solution. In contrast to number average molecular weight, these methods sum the weight fraction of each species multiplied by their molecular weight. It is expressed mathematically as

$$\overline{M_w} = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

In measurements of colligative properties, each molecule contributes equally regardless of weight; whereas with light scattering, the larger molecules contribute more because they scatter light more effectively. Hence, weight average molecular weights are always higher than number average molecular weights, except, when all molecules are of the same weight; then $M_w = M_n$. The narrower the molecular weight range, the closer are the values of M_w and M_n, and the ratio M_w/M_n may thus be used as an indication of the breadth of the molecular weight range in a polymer sample. This ratio is called the polydispersity index. If all the polymer molecules present have the same molecular weight, the system is monodisperse. The degree of polymerization of a polymer can be expressed as the ratio of molecular weight of the polymer to that of the monomer.

Molecular weight of polymers can also be measured based on viscosity measurement and is known as viscosity average molecular weight $(\overline{M_v})$. It is expressed as

$$\overline{M_v} = \left(\frac{\sum NiM_i^{1+a}}{\sum N_i M_i} \right)^{1/a}$$

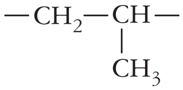
where a is a constant that depends on the polymer/solvent pair used in the viscosity experiments. When $a = 1$, $\overline{M_v}$ is equal to the weight average molecular weight, $\overline{M_w}$. For other values of a, $\overline{M_v}$ is between weight average and number average molecular weight.

Problem 1

If average degree of polymerization of polypropylene is 2×10^4*, calculate the weight average molecular weight of the polymer.*

Solution

The repeat unit in polypropylene is:



$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

Molecular weight of repeat unit is 42 g/mol. We know that

$$\text{Molecular weight of polymer} = \text{Molecular weight of repeat unit} \times \text{Degree of polymerization}$$

Therefore,

$$\text{Molecular weight of polymer} = 42 \times 2 \times 10^4 = 84 \times 10^4 = 8.4 \times 10^5 \text{ g/mol}$$

Problem 2

When 52 g of styrene was polymerized, average degree of polymerization was found to be 1.5×10^5*. Calculate the number of styrene molecules in the original sample and number of molecules of polystyrene produced.*

Solution

The number of molecules of styrene in 52 g is found as

$$\text{Number of molecules of styrene} = 52 \times \frac{6.023}{104} \times 10^{23} = \frac{6.023}{2} \times 10^{23}$$

Number of polystyrene molecules formed is

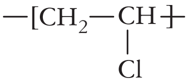
$$\frac{\text{Number of styrene molecules}}{\text{Degree of polymerization}} = \frac{6.023 \times 10^{23}}{2} \times \frac{1}{1.5 \times 10^5} = \frac{6.023 \times 10^{23}}{3 \times 10^5} = 2.008 \times 10^{18} \text{ molecules}$$

Problem 3

Calculate the degree of polymerization of vinyl chloride if the number average weight of polymer is 1.31×10^5 *g/mol.*

Solution

The structure of repeat unit in polyvinyl chloride is



$$-[CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}]-$$

Molecular weight of repeat unit = 62.5 g/mol.
Molecular weight of polymer = 1.31×10^5 g/mol.
Therefore, degree of polymerization is

$$\frac{\text{Molecular weight of polymer}}{\text{Molecular weight of repeat unit}} = \frac{1.31 \times 10^5}{62.5} = 2000$$

Problem 4

A polymer has the following composition: 100 molecules of molecular mass 1000 g/mol, 200 molecules of molecular mass 2000 g/mol and 500 molecules of molecular mass 5000 g/mol. Calculate the number and weight average molecular weight and the polydispersity index.

Solution

Given that M_1 = 1000 g/mol, N_1 = 100; M_2 = 2000 g/mol, N_2 = 200; M_3 = 5000 g/mol, N_3 = 500.

The number average molecular weight in given by:

$$M_\text{n} = \frac{\sum N_i M_i}{\sum N_i} = \frac{100 \times 1000 + 200 \times 2000 + 500 + 5000}{100 + 200 + 500} = \frac{1 \times 10^5 + 4 \times 10^5 + 25 \times 10^5}{800}$$

$$= 3.75 \times 10^3 \text{ g/mol}$$

The weight average molecular weight is given by:

$$\overline{M}_\text{w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{100 \times (1000)^2 + 200 \times (2000)^2 + 500 \times (5000)^2}{30 \times 10^5}$$

$$= \frac{1 \times 10^8 + 8 \times 10^8 + 125 \times 10^8}{30 \times 10^5} = \frac{134 \times 10^8}{30 \times 10^5} = 4.46 \times 10^3 \text{ g/mol}$$

The polydispersity index (PDI) is

$$\frac{\overline{M_\text{w}}}{\overline{M_\text{n}}} = \frac{4.46 \times 10^3}{3.75 \times 10^3} = 1.19$$

Concept Check

- Discuss the relationship between molecular weight and the various properties of polymers.
- What is number average molecular weight? How is it expressed mathematically?
- How is weight average molecular weight determined and expressed?
- What is polydispersity index?

10.6 Structure–Property Relationship of Polymers

The structure of the polymer depends on the (a) size and shape of the polymer chain and (b) chemical nature of the monomers. The structure of the polymers further affects the physical and mechanical properties of polymers.

Strength

Melt viscosity (the resistance of molten polymer to shear deformation), impact and tensile strength are a few mechanical properties of a polymer. Tensile strength and impact strength increase with molecular mass up to a certain point and then become constant {Figure 5(a)}. The melt viscosity of the polymer initially shows a gradual increase with the molecular mass and steep increase at higher molecular masses {Figure 5(b)}. For a polymer to be commercially useful, it should have low-melt viscosity, high tensile and impact strength.

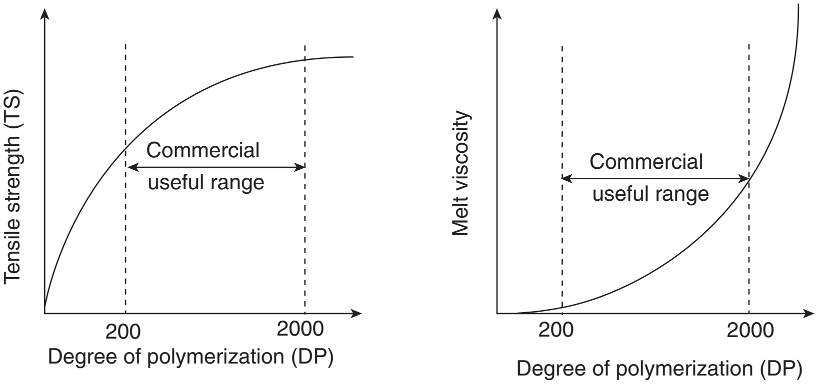


Figure 5 Relationship of degree of polymerization with (a) tensile strength and (b) melt viscosity.

Crystallinity

Polymers usually consist of crystalline and amorphous parts. The requirement for a polymer to crystallize is regularity of molecular structure with greater symmetry, such that polymer chains can pack up closely in an ordered structure.

The degree of crystallinity of the polymer depends on its structure. For example, a linear polymer will have high crystallinty, because the atoms along the chain permit closer approach, which drops sharply with branching. This further drops sharply with bulky pendant group in polymer chain. For example, linear polymer like HDPE is more crystalline than LDPE (i.e., branched polyethylene). LDPE is more crystalline than polystyrene (where a bulky group like benzene is attached to the carbon atom).

The density of crystalline polymer is greater than that of a non-crystalline polymer because of more efficient packing in the former. From density measurement, it is possible to determine the degree of crystallinity by using the formula:

$$\text{Degree (or percentage) of crystallinity} = \frac{d_c/(d_c - d_a)}{d_s/(d_c - d_a)} \times 100$$

where d_c is the density of crystalline polymer, d_a is the density of amorphous polymer and d_s is the density of specimen whose crystallinity is to be detremined.

The polymer chains with polar groups can form hydrogen bonds with their neighboring chains and have high crystallinity. For example, nylon-6,6 with high degree of crystallinity has high tensile and impact strength.

Crystallinity of a polymer also depends on the stereo-regular arrangement. Polymers like isotactic and syndiotactic polystyrene, etc., are highly crystalline. On the other hand, atactic polystyrene, in which the substituents are arranged in a random manner, are less crystalline.

Elasticity

Elasticity of a polymer material is mainly because of the uncoiling and recoiling of the molecular chains on application of force. For a polymer to show elasticity, the individual chains should not break on prolonged stretching. Breaking takes place when the chains slip past each other and get separated. This is avoided by molecular engineering such as

1. Introducing cross-linking at suitable molecular position.
2. Avoiding bulky side group such as aromatic and cyclic structure in the repeat units.
3. Introducing more non-polar groups in the chains so that the chains do not separate on stretching.

In other words, to get an elastomeric material, any factor that introduces crystallinity should be avoided.

Non-elastic Nature of Fibers

In contrast to elastomers, the high strength and non-elastic nature of the fibers is attributed to its crystallizability on pulling. In fibers, the chain mobility is reduced by very close packing of the polymer chain backbone without cross-linking. Polar groups and aromatic and cyclic rings in the backbone chain are known to impart a high strength to the polymer fiber. For example, polyamide (nylon-6,6), polyethylene terephthalate (terylene).

Plastic Deformation

Plastic deformation or flow behavior of polymers can be studied by applying heat and pressure on the polymer materials. Thermoplastic polymers on application of heat and pressure, initially become soft, flexible and undergo deformation. On further heating above their melting point (T_m) they melt and flow. Such a property is called plastic deformation. On cooling, they return to their original state. This type of plastic deformation is used in molding operation.

Thermoplastics exhibit plastic deformation because they are linear, closely packed and the individual chains are held by secondary forces such as van der Waal's force, hydrogen bonding and dipole–dipole interactions. On the other hand, thermosetting polymers do not exhibit plastic deformation, because they undergo cross-linking during molding to form three-dimensional structure materials. All the monomer units are held together through strong primary covalent bonds throughout the structure. These covalent bonds cannot be easily broken by just heating. On strong heating, charring (degradation) occurs instead of plastic deformation. Therefore, thermosetting polymers do not undergo reversible plastic deformation.

Chemical Resistivity

The chemical resistance of a polymer depends on the structure of the polymer and also on the nature of attacking reagent. When the chemical attacks on the polymer, it first softens, swells and loses its strength, and then it dissolves. Chemical resistivity of polymers depends on a number of factors such as presence of polar and non-polar groups, the molar mass, degree of crystallinity, extent of cross-linking, etc.

Polymers containing polar groups like –OH or –COOH are soluble in polar solvents such as water, alcohol, etc. Polymers with non-polar groups such as $–CH_3$, $–C_6H_5$ swell easily and dissolve in non-polar solvents such as benzene, toluene and carbon tetrachloride, etc. Polymers containing ester groups (polyester) undergo hydrolysis with strong alkalis at high temperatures. Polyamide like nylon containing –NHCO– group, polyurethane contain –NHCOO– group can be attacked by strong acids or alkalis.

Higher the molecular mass of the polymer, the dissolution decreases. Chemical resistance of a polymer increases with increase in crystallinity. Similarly, chemical resistance increases with degree of cross-linking.

Glass Transition Temperature (T_g)

The temperature below which a polymer is hard, brittle and above which it is soft and flexible is called the glass transition temperature, and it is denoted by T_g. The hard, brittle state is known as the glassy state and the soft flexible state is called the rubbery state. In the glassy state, there is no segmental and molecular motion. On the other hand, in rubbery state, there is only segmental motion but no molecular mobility.

Factors Affecting T_g

1. **Flexibility:** Linear polymer chains made of C–C, C–O or C–N single bonds have a higher degree of freedom of rotation on a single bond. Presence of rigid groups, such as aromatic and cyclic groups or bulky groups, in the carbon chain backbone hinders the freedom of rotation. This restriction in the chain mobility increases the T_g value. For example,
   - In a linear polymer like polyethylene, $T_g = -110°C$.
   - In polyethylene terephthalate with cyclic group in the carbon chain backbone, $T_g = 69°C$.
   - In polystyrene with aromatic group attached to one of the carbon atoms in the carbon chain backbone, $T_g = 100°C$.
2. **Effect of side group:** Poly [α-methyl styrene] has higher T_g (170°C) value while polystyrene has lower T_g (= 100°C) value, due to the presence of extra methyl side group in the former which hinders the free rotation about carbon–carbon bond of carbon chain backbone. This restricts the chain mobility and thereby increases the T_g value.
3. **Intermolecular forces:** Presence of a large number of polar groups in the molecular chain lead to strong intermolecular cohesive forces, which restrict the segmental/molecular mobility. This leads to an increase in T_g. For example, polypropylene ($T_g = -18°C$) has lower T_g compared to nylon-6,6 ($T_g = 57°C$).
4. **Branching and cross-linking:** A small amount of branching will reduce the value of T_g, because the free volume increases with branching and thus decreases the T_g. On the other hand, a high density of branching (cross-linking) brings the polymer chains closer, lowers the free volume and thus reduces the chain mobility, thereby increasing the value of T_g. For example, LDPE has lower value of T_g as compared to cross-linking low-density polyethylene (XLDPE).
5. **Presence of plasticizers:** Addition of plasticizers reduces the T_g value. For example, diisooctyl phthalate, which is added to PVC reduces its T_g from 80°C to below room temperature.
6. **Stereo-regularity:** The T_g increases with the stereo-regularity of polymers. Thus, T_g of a isotactic polymer is greater than that of a syndiotactic polymer, which in turn has greater T_g than an atactic polymer.
7. **Molecular weight**: The T_g of all polymers, in general, increases with molecular weight up to 20,000; and beyond this the effect is negligible.

Significance of T_g

1. The T_g value is a measure of flexibility of a polymer and the type of response the polymer would exhibit to mechanical stress.
2. Its value gives an idea of thermal expansion, heat capacity, refractive index, electrical and mechanical properties of the polymer.

3. Its value can decide whether a polymer at the use temperature will behave like rubber or plastic.
4. Knowledge of T_g and T_m is useful in choosing the right temperature for fabrication of materials. Crystalline melting temperature (T_m) is the temperature at which sufficient thermal energy is available to disrupt the ordered structure of crystalline polymers. (Fabrication temperature is the region in which the polymer material can be converted into a finished product through different processing techniques, such as injection molding, compression molding, calendering, extrusion, etc.).

Concept Check

- Discuss the relation between mechanical strength and degree of polymerization of a polymer.
- Discuss the structure–property relationship of polymers with respect to:
  a. elasticity.
  b. plastic deformation.
- What is the effect of the structure of a polymer on its crystallinity?
- Discuss the relation between the structure of a polymer and its chemical sensitivity.
- What is glass transition temperature? Discuss its significance.
- List the various factors affecting glass transition temperature and discuss the effect of branching and cross-linking.

10.7 Plastics

Plastics are polymers of either natural or synthetic organic compounds with high molecular mass. They may contain added substances to improve their properties and performance. The word *plastic* is derived from the Greek word "plastikos", which means *capable of being shaped or molded*. The use of this name refers to the "plasticity" of these materials during manufacture. This allows them to be cast, pressed or extruded into a variety of shapes. Plastics are used in the manufacture of a variety of industrial products or varied forms, such as films, fibers, plates, tubes, bottles, boxes, etc. In the recent times, plastics have entered into every possible sphere of our lives right from our home front to the warfront, and from our kitchen to industries.

Properties and Uses of Plastics as Engineering Materials

The use of plastics as an engineering material has grown tremendously because of their several advantages over other conventional materials. These include properties such as light weight, high strength-to-weight ratio, chemical and corrosion resistance, low thermal and electrical conductivities, etc. The following are some of the important properties, which make plastics more useful in practice than any other conventional material.

1. Plastics possess low specific gravity varying from 0.94 to 1.6, which is much less than that of metals and alloys.
2. Their strength per unit weight is much greater than those of metals.
3. They can be fabricated into any desired shape and their cost of fabrication and maintenance is low. They do not require any protective coating such as paints.
4. They possess low coefficient of thermal expansion and are very good thermal and electrical insulators.
5. They are chemically inert to the action of light, oils, acids and dampness. Hence, they are more resistant to corroding agents such as gases, water, salts, oxidizing agents, etc. Therefore, they are more durable than metals.

6. Some plastics are highly transparent and exhibit high refractive index.
7. They can be easily molded with accurate dimensions even into intricate and complicated forms and shapes.
8. They possess good shock absorption capacity. Some plastics absorb shocks even better than steel.
9. They possess high resistance to abrasion.
10. They have the ability to take variety of colors, shades and excellent finish. Their colors/shades do not fade easily.
11. Polymer adhesives are quite strong and durable.
12. Some polymers can also conduct electricity as good as metals. They are called intrinsically conducting polymers.

Some important uses of plastics arising from their characteristic properties are discussed as follows:

1. Due to light weight and high tensile strength, plastics are used in aircraft, automobiles and structural industries.
2. Due to high resistance to wear and tear, they are used as gears, pulleys and self-lubricants.
3. Due to hardness and good shock-absorbing capacity, they are used in machines to reduce noise and vibration.
4. Due to good thermal resistance, they are used for making handles of hot objects such as electric iron, soldering, frying pans, pressure cookers, etc.
5. Due to chemical inertness and high resistance to corrosion, they are used in chemical industries as components for chemical plants. For example, PVC is used in place of stainless steel for tubes, pipes for underground installations, tanks, absorption towers, etc.
6. With low electrical conductivity and good insulation properties, plastics find application in electrical components/appliances such as plugs, switches, holders, radio, TV circuits, cabinets and also in electronic industries.
7. High optical clarity and transparency make plastics find application in optical lenses, wind screens of automobiles, etc.
8. Good adhesion property makes them useful in laminated wood products, paints, varnishes, etc.
9. Heat and sound dampening property makes plastics useful in cold storage refrigeration, and air-conditioning buildings, theatres, auditoriums, etc.
10. Good abrasion resistance makes them useful in water hoses, water tubes, floor tiles, telephone parts, gramophone records, etc.
11. Their ability to be made in a variety of colors makes them useful for making household articles such as combs, toys, trays, chairs, containers, etc.

Classification of Plastics

Plastics may be classified based on a number of criteria, such as chemical structure, processes used in their synthesis and chemical or physical properties. Based on the molecular units that make up the polymer's backbone and side chains, plastics may be classified as acrylics, polyesters, silicones, polyurethanes and halogenated plastics. Based on the chemical process of manufacture, they may be classified as condensation, poly-addition, or cross-linking plastics. Most commonly, plastics are classified based on qualities that are important for manufacturing or product design, that is, as thermoplastic and thermosetting polymers.

1. **Thermoplastic polymers:** These are plastics which become soft on heating and hard on cooling. The process of heating and cooling can be repeated for a number of times without affecting their

properties. They undergo reversible changes on heating and cooling. For example, polyethylene; PVC; teflon; nylon-6,6; etc.

2. **Thermosetting polymers:** These are plastics which undergo chemical changes and cross-linking on heating and become permanently hard, rigid and infusible on cooling. They undergo irreversible changes on heating. For example, phenol–formaldehyde (bakelite), urea–formaldehyde, epoxy resin, etc. The distinguishing characteristics of thermoplastic and thermosetting polymers are given in Table 2.

Table 2 Differentiate between thermoplastics and thermosetting polymers

Thermoplastic Polymer	*Thermosetting Polymer*
They are mostly formed by addition polymerization	They are formed by condensation polymerization
They exhibit linear long-chain structures with negligible cross-links	They have three-dimensional network structure joined by strong covalent bonds
They undergo reversible changes on heating	They undergo irreversible changes on heating and degrade
They consist of polymers of low molecular weight	They consist of polymers of high molecular weight
They are soft, weak and less brittle	They are hard, strong and more brittle
They are soluble in organic solvents as their intermolecular bonds are weaker	They are insoluble in almost all organic solvents as their intermolecular bonds are stronger and they are cross-linked
They readily soften on heating due to breaking of the secondary bonds between the individual chains	They do not soften on heating as their bonds retain strength. However, prolonged heating causes degradation of polymers
By heating to suitable temperatures, they can be softened, reshaped and reused	They retain their shape and structure even on heating. Hence, they cannot be reshaped and reused
There is no change in chemical composition and structure during molding process	They undergo chemical changes, such as further polymerization and cross-linking during molding process

10.8 Some Important Commercial Thermoplastics

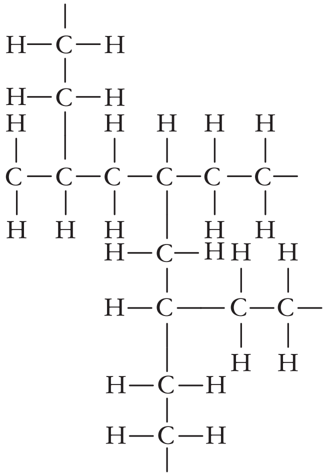
Polyethylene (PE)

Polyethylene is a homopolymer of ethylene produced by addition polymerization, but today most polyethylenes are copolymers of ethylene with 1–10% of α–olefins, such as 1-butene, 2-methyl pentene, 1-hexene and 1-octene. LDPE and HDPE are the homopolymers of ethylene. LDPE is a branched polymer with only 40–60% crystallinity. HDPE is predominantly linear with no or small amount of branching and high crystallinity up to 90%. Linear low density polyethylene (LLDPE) is a linear polymer with significant number of branches.

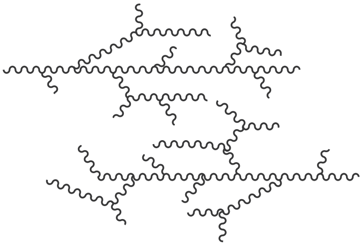
LDPE

LDPE is a linear polymer with branching. It is manufactured under high pressure (1000–3000 atm) and in the temperature range of 80–350°C using initiators such as benzoyl peroxide or oxygen. The process may be operated continuously or batchwise in an autoclave.

$$\underset{\text{Ethylene}}{n\mathrm{CH_2{=}CH_2}} \xrightarrow[\text{High pressure}]{\text{Benzoyl peroxide}} \underset{\text{Polyethylene}}{\left[\mathrm{CH_2 - CH_2}\right]_n}$$



LDPE: polymer molecules have lots of branching



Molecules unable to pack together very closely

Properties:

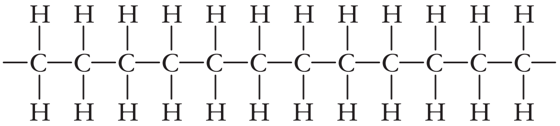
1. It is a white waxy and translucent material which floats in water.
2. It has the density in the range of 0.915–0.94 g/cm^3.
3. It melts in the temperature range 107–120°C. Its T_g value is −120°C.
4. It is flexible and tough over a wide temperature range.
5. It is chemically inert and has good resistance to acids and alkalis.
6. It exhibits high impact strength, low brittleness temperature, film transparency and outstanding electrical insulation properties.

Applications: LDPE is extensively used in the manufacturing of transparent films for food and garments packaging. It is also used in the production of squeeze bottles, paper coatings, wrappings, table cloths, industrial containers and sheets. It is also used in cable and wire insulations.

HDPE

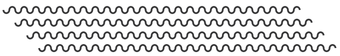
HDPE is a linear polymer with little or no branching. It is produced under low pressure using Ziegler–Natta catalyst (triethylaluminium and titanium tetrachloride) by coordination polymerization or using metal oxide catalyst by Phillips process. The reaction is carried out below 100°C.

$$\underset{\text{Ethylene}}{n\mathrm{CH_2{=}CH_2}} \xrightarrow[\text{Low pressure}]{\text{Ziegler–Natta catalyst}} \underset{\text{Polyethylene}}{\left[\mathrm{CH_2 - CH_2}\right]_n}$$



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$$

HDPE: polymer molecules have little or no branching



Molecules able to arrange themselves in very close proximity

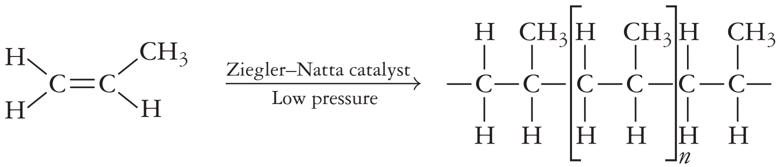
Properties:

1. It has higher density than LDPE, in the range 0.945–0.965 g/cm^3.
2. It melts in the temperature range 130–138°C. Its T_g value is –20°C.
3. It has greater rigidity than LDPE.
4. It has better chemical resistance than LDPE.
5. It also exhibits better stiffness, toughness, good tensile strength, hardness and heat resistance properties.
6. It is opaque and has less impact strength but better barrier properties than LDPE.

Applications: HDPE is used in the manufacture of dustbins, milk bottles, cans, drums, containers, fuel tanks, corrugated pipes, wire and cable insulations.

Polypropylene

Polypropylene (PP) is a linear hydrocarbon polymer containing little or no unsaturation. PP is manufactured at low pressure using Ziegler–Natta catalysts (aluminium alkyls and titanium halides) by coordination polymerization. Usually 90% or more of the polymer is in the isotactic form. The isotactic PP is a stereospecific polymer in which the propylene units are attached in a head-to-tail fashion, and the methyl groups are aligned on the same side of the polymer chain. Hence, isotactic PP cannot crystallize in the same fashion as PE, since steric hindrance by the methyl groups prohibits this conformation.



Propylene

Polypropylene

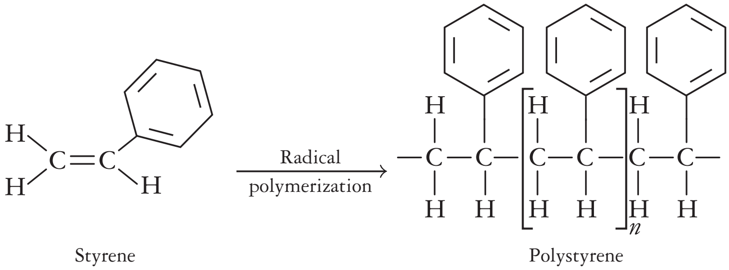
Properties:

1. Isotactic PP has density around 0.90 g/cm^3.
2. It melts in the temperature range 165–170°C.
3. The electrical properties of PP are similar to PE.
4. It is inert to water and microorganisms and it is a low-cost polymer.

Applications: The major products manufactured using PP are filaments and fibers, automotive and appliance components, packaging containers, furniture and toys. PP films are used as pressure-sensitive tapes, revertible pouches and shrink films.

Polystyrene

Polystyrene (PS) homopolymer is manufactured by bulk or suspension polymerization of styrene monomer using free radical initiators.



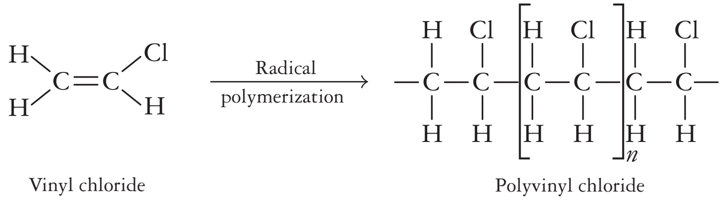
Properties:

1. It is a rigid, transparent thermoplastic which emits a characteristic metallic ring when dropped.
2. It is a rigid amorphous polymer with density of 1.05 g/cm^3.
3. It offers good stiffness and dimensional stability.
4. It has excellent moisture resistance property.
5. It possesses good electrical insulation property, good colorability and moldability.

Applications: PS is used in the manufacturing of household wares, such as combs, toys, buttons, radio and television parts. It is also used in the production of video cassettes, refrigerator parts, machine housings, blister packs and high frequency electrical insulation material.

Polyvinyl Chloride

Polyvinylchloride (PVC) is produced by free-radical initiated chain polymerization. About 80% of the PVC is manufactured by suspension, about 10% by bulk and remaining by emulsion polymerization. The polymerization is usually carried out in the temperature range 50–75°C. PVC is the most versatile of all plastics because of its blending capability with plasticizers, stabilizers and other additives.



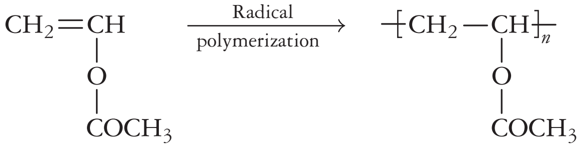
Properties:

1. It is a colorless, odorless, non-flammable and chemically inert polymer.
2. It is resistant to light, atmospheric oxygen, inorganic acids and alkalis.
3. It possesses greater stiffness and rigidity compared to polyethylene.

Applications: Approximately 60% of PVC is used in building and construction, mainly in rigid pipes, flooring and vinyl siding. Plasticized PVC is used mainly in wire and cable insulations and in packaging. Flexible films and sheets are used as pool liners and roof coatings. PVC plastisols are used in flooring, artificial leather, wall coverings and carpet backing. Other important applications are pipe fittings, electrical outlet boxes and parts for automotive bumpers.

Polyvinyl Acetate

Polyvinyl acetate (PVA) is the starting material for polyvinyl alcohol, polyvinyl butyral and polyvinyl formal. It is manufactured by free-radical initiated emulsion polymerization of vinyl acetate monomer. The polymerization is carried out at 70°C. PVA is usually used in the form of emulsion.



$$\begin{array}{c}\mathrm{CH_2{=}CH}\\ |\\ \mathrm{O}\\ |\\ \mathrm{COCH_3}\end{array} \xrightarrow[\text{polymerization}]{\text{Radical}} \begin{array}{c}\mathrm{-\!\!\left[CH_2-CH\right]_{\mathit{n}}\!\!-}\\ |\\ \mathrm{O}\\ |\\ \mathrm{COCH_3}\end{array}$$

Vinyl acetate Polyvinyl acetate

Properties:

1. PVA is too soft and shows excessive "cold flow" for use in molded plastics.
2. It is an atactic amorphous polymer which is transparent if free from emulsifier (refractive index of 1.47).
3. The density of PVA is 1.191g/cm^3 and T_g value is 28–31°C.
4. A random copolymer with ethylene, poly (ethylene-covinyl acetate), has greater flexibility and greater acceptance of filler over PE.

Applications: PVA is used as latex emulsion for the manufacturing of interior and exterior paints, as adhesives for textiles, paper and wood as sizing material.

Polytetrafluoroethylene/Teflon

Teflon is a linear polymer without branching. It is usually manufactured by emulsion polymerization of tetrafluoroethylene (TFE) using peroxide or ammonium persulphate as initiators.

$$\underset{\text{TFE}}{n\mathrm{CF_2{=}CF_2}} \xrightarrow[\text{Peroxide as initiator}]{\text{Emulsion polymerization}} \underset{\text{PTFE}}{-\!\!\left[\mathrm{CF_2-CF_2}\right]_n\!\!-}$$

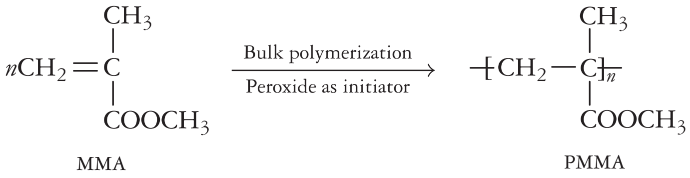
Properties:

1. It is a highly crystalline polymer (93–98%).
2. It has high melting temperature (T_m = 327°C), high temperature stability and low temperature flexibility.
3. It has low coefficient of friction and remains slippery over a wide range of temperature (–40–300°C).
4. It is practically insoluble in any solvent and is not wetted by either oil or water.
5. It has excellent electrical insulating properties.

Applications: Teflon is used for insulation of motors, generators, transformers, coils, capacitors, wires and cables. It is used as coating on food processing equipment such as bakery trays, frying pans because it is not wetted by oil or water. It is also used for coating on army weapons as an anticorrosive coat. It is used in gaskets, industrial filters, belts which are subjected to wear at elevated temperatures and in non-lubricated bearings. It is also used as a dry lubricant since it remains slippery over a wide range of temperatures. It is used as cardiovascular grafts, heart patches and ligaments for knees.

Polymethyl Methacrylate/Plexiglass

Plexiglass (PMMA) is obtained by the polymerization of methylmethacrylate (MMA) using hydrogen peroxide as initiator by bulk or suspension polymerization.



$$nCH_2{=}\underset{\substack{| \\ COOCH_3}}{\overset{\substack{CH_3 \\ |}}{C}} \xrightarrow[\text{Peroxide as initiator}]{\text{Bulk polymerization}} \left[CH_2-\underset{\substack{| \\ COOCH_3}}{\overset{\substack{CH_3 \\ |}}{C}}\right]_n$$

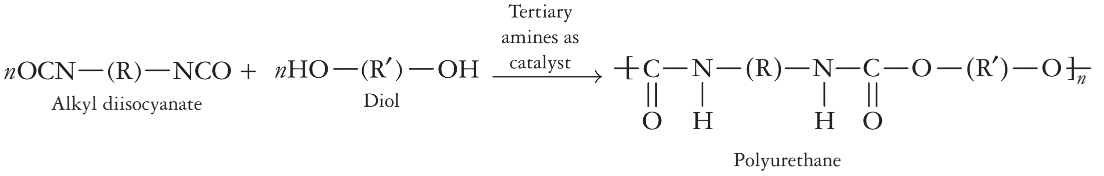
Properties:

1. It is an amorphous and transparent plastic.
2. It has good optical clarity (refractive index = 1.4), but poor scratch resistance.
3. It is resistant to water, alkalis and inorganic salts but dissolves in organic solvents.
4. It has good outdoor weathering property and dimensional stability.
5. It is tougher than polystyrene.

Applications: PMMA is used for making automobile-lamp housing, street-light housing, aircraft windows, canopies and signal boards. It is used in paints and adhesives. It is also used for making artificial teeth and contact lenses; laser disks and DVDs; and transparent bath tubs and wash basins.

Polyurethanes

Polyurethanes (PU) are the polymeric materials in which the monomer units are linked through –NHCOO– group. They are prepared by the polyaddition reaction between diisocyanate and diols or triols or polyols. PU resembles polyamides in their structure, with the presence of one more oxygen making the chain more flexible.



$$nOCN-(R)-NCO + nHO-(R')-OH \xrightarrow{\text{Tertiary amines as catalyst}} \left[\underset{\substack{\| \\ O}}{C}-\underset{\substack{| \\ H}}{N}-(R)-\underset{\substack{| \\ H}}{N}-\underset{\substack{\| \\ O}}{C}-O-(R')-O\right]_n$$

During addition reaction, the H atom of OH group migrates and adds to nitrogen atom; hence it is called rearrangement addition polymerization.

Properties:

1. The presence of additional oxygen in the chain increases the flexibility and thus reduces the T_m of PU to 150°C (T_m of nylon-6 is 250°C).
2. It is resistant to water, oil and corrosive chemicals.
3. It may be translucent or opaque.
4. It has high tensile strength and crystallizes on stretching.
5. It has excellent abrasion resistance.

Applications: PU coatings are used as gymnasium and dance floors where high abrasion resistance is required. They are also used as surface coatings, films, foams and as adhesives. PU foams are used as cushions for furniture and automobiles because of improved strength, lower density and easier fabrication. PU fabrics are used as lightweight garments and swimsuits because of their stretching property. PU is used as soles for shoes. PU elastomers are used as gaskets, seals, tyres and industrial wheels.

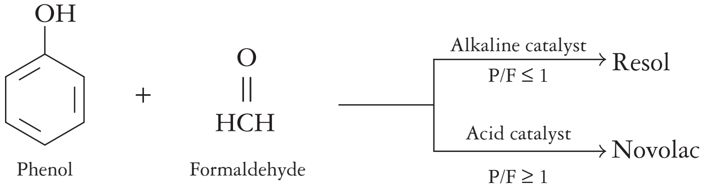
Concept Check

- Discuss the distinguishing features of LDPE and HDPE.
- What are polyurethanes? List their important uses.
- Discuss the structure of PTFE. Explain its important uses based on properties.
- Explain the use of plexiglass in optical lenses.

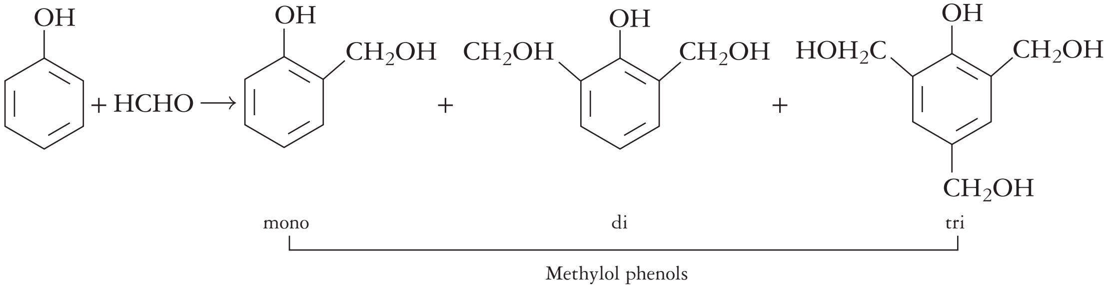
10.9 Some Important Commercial Thermosetting Resins

Phenol–Formaldehyde Resins

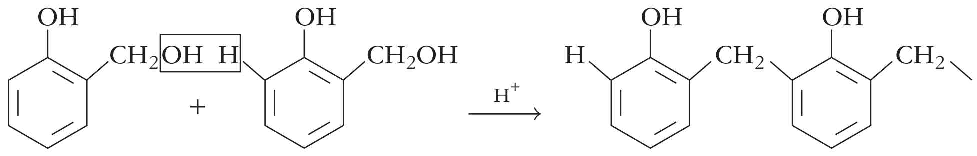
Phenol–formaldehyde (PF) resins are prepared by the condensation reaction between phenol and formaldehyde using acid or base as catalyst. The nature of the product formed depends on the relative concentrations of phenol and formaldehyde and also on the type of catalyst used.



When the phenol reacts with formaldehyde, we may get monomethylol, dimethylol or trimethylol phenol depending on the phenol-to-formaldehyde ratio.

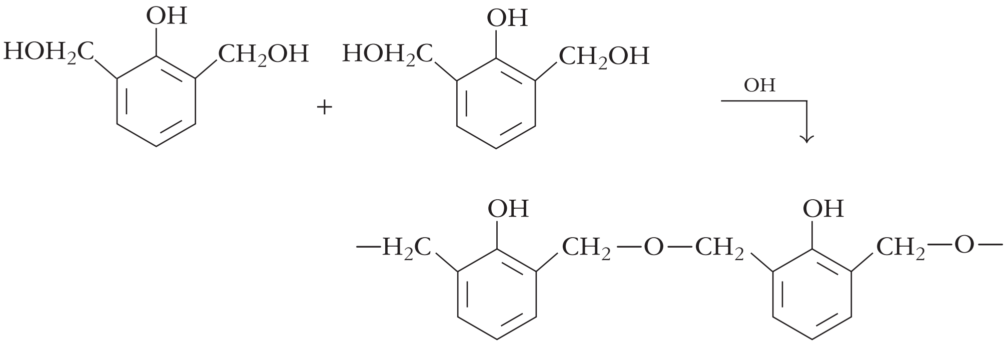


A large excess of phenol on heating with an aqueous solution of formaldehyde in the presence of acid catalyst gives a polymer called **novalac resin**. Novolacs are phenol–formaldehyde resins made when the molar ratio of formaldehyde to phenol is less than 1. They are linear polymers with low molecular weight.



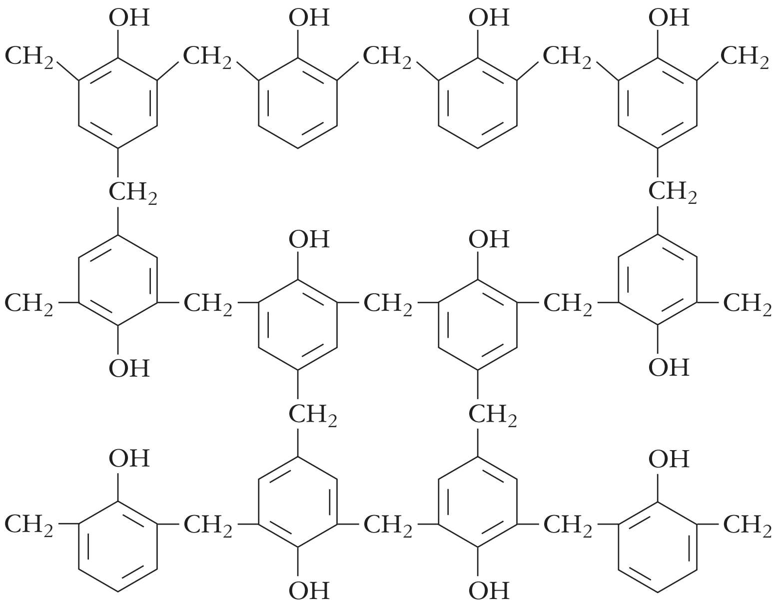
Novolac

On the other hand, a large excess of an aqueous solution of formaldehyde on heating with phenol in the presence of base as catalyst gives polymer called **resol**. These resins are made with a formaldehyde-to-phenol ratio greater than 1 (usually around 1.5).



Resol

Whereas further cross-linking of novolac resin can be done by adding excess of formaldehyde and heating, resols can be converted into final cured product merely by heating. Both the resins on curing (with wood flour filler) give highly cross-linked product called **Bakelite**.



Bakelite

Properties:

1. Bakelite is a rigid, hard, scratch resistance material.
2. It shows good electrical insulation property.
3. It has thermal stability of up to 200°C and good dimensional stability.
4. It is resistant to water and shows low flammability.

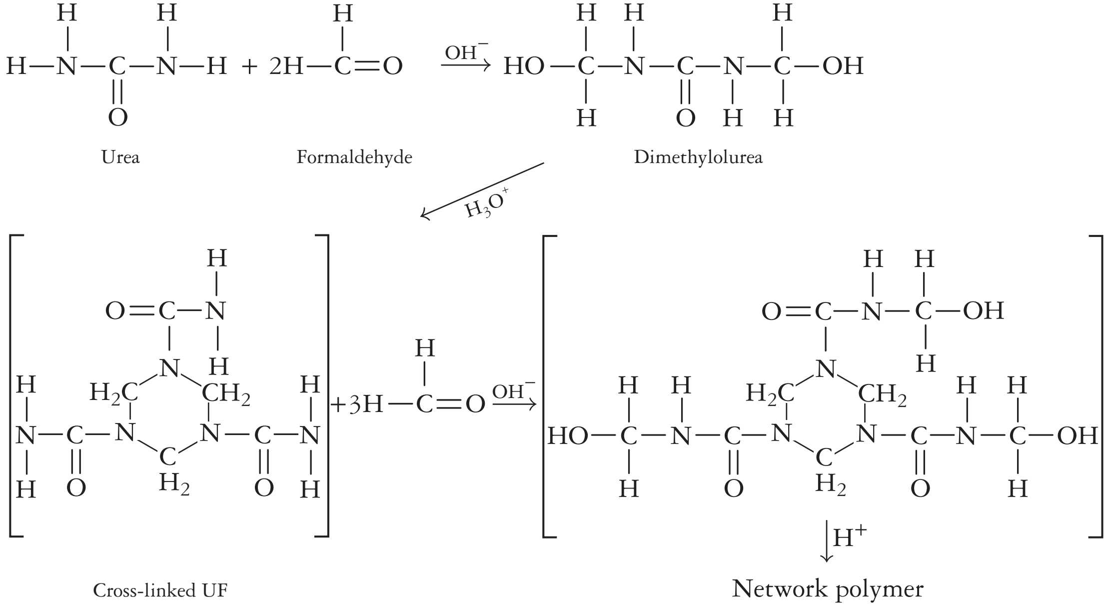
Applications: PFs are used for making electrical equipment parts such as switches, plugs, switchboards, cooker handles, welding tongs, electric iron parts and telephone parts. Due to its hardness, it is used for making golf ball and heads for typewriters. It is used as hot-setting adhesives for plywood, cement for sealing electric bulbs to their metal holders and for lamination of paper, cardboards and wood.

Amino Resins

The term aminoplastics refers to polymers produced by interaction of amines or amides with aldehydes. Of the various polymers of this type there are two commercially important ones, namely, urea–formaldehyde and the melamine–formaldehyde resins.

Urea–Formaldehyde Resin

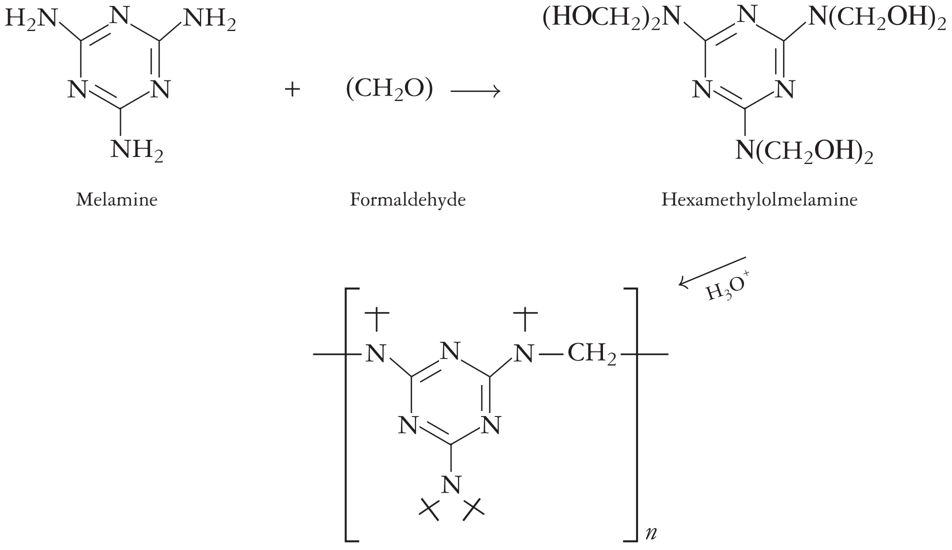
Urea–formaldehyde (UF) resin is produced by the condensation of urea with formaldehyde by two-stage reaction. In the first stage, formaldehyde reacts with urea under neutral or mildly alkaline conditions to produce monomethylol and dimethylol ureas. The ratio of monomethylol to dimethylol compounds will depend on the urea-to-formaldehyde ratio, and it is important that there should be enough formaldehyde to allow some dimethylol urea formation. In the second stage, it undergoes further condensation with free amino groups of urea to produce resinous cross-linked UF.



Applications: UF resins are used as adhesives for the particle board, plywood and furniture industries and as casting material in textile finishing. UF foams are used as an aid to floral decoration and in ground form as an artificial snow in cinema and television productions.

Melamine–Formaldehyde Resin

Reaction of melamine with neutralized formaldehyde at about 80–100°C leads to the production of a mixture of water-soluble methylol melamines. These hydroxyl methyl derivatives can process up to six methylol groups per molecule and include trimethylol melamine and hexamethylol melamine. The methylol content of the mixture will depend on the melamine formaldehyde ratio and on the reaction conditions. On further heating, the methylol melamines condense and a point is reached where hydrophilic resin separates out on cooling. The condensation reaction is strongly dependent on the pH.



Melamine

Formaldehyde

Hexamethylolmelamine

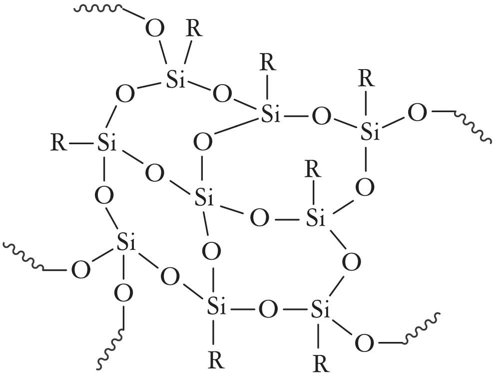
Cross-linked MF

Properties: MF is hard, scratch resistant, fairly heat resistant and free from color with wide colorability.

Applications: The principal application of MF compounds is in the manufacture of tableware. Cellulose-filled compounds find usage in outlet for trays, clock cases and radio cabinets. Mineral-filled powders are used in electrical applications and knobs and handles for kitchen utensils. It is used in laminating applications as bonding agent and also as hot-setting adhesives. MF condensates are used in textile finishing as permanent glazing agents, rot-proofing agents, in wool shrinkage control and also as flame-proofing agents.

Silicone Resins

Silicone resins are a type of silicone material prepared by hydrolytic condensation of various silicone precursors with the general formula of $R_nSiX_mO_y$, where R is a non-reactive substituent, usually methyl or phenyl and X is a functional group such as H, OH, Cl. Various chlorosilanes have been used as starting materials. To get highly cross-linked networks, a small quantity of trichlorosilanes must be incorporated into the blend.



R = Me, OH, H

Properties: Silicone resins have very good heat resistance property and are good electrical insulators, particularly at elevated temperatures and under damp conditions.

Applications: Methyl–phenyl silicone resins are used in the manufacture of heat-resistant glass cloth laminates, pressure-sensitive adhesives, silicone rubbers, coatings and additives.

Concept Check

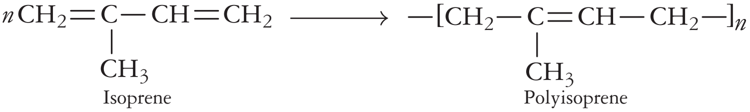
- What are phenol–formaldehyde resins? How are they synthesized?
- Discuss the structure, properties and applications of Bakelite.
- Explain the steps involved in the preparation of urea–formaldehyde resins. Give the structure of cross-linked and networked polymers.
- Discuss the structure and applications of melamine–formaldehyde resins.

10.10 Elastomers (Rubbers)

Elastomers are polymers which undergo very long elongation (500–1000%) when subjected to an external force, but readily regain their original position when external force is removed. This property of elastomers is called *elasticity*. This arises due to coiled structure of elastomers. Elastomers can be classified as natural and synthetic.

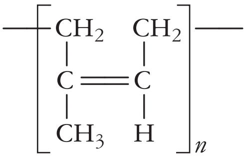
Natural Rubber (NR)

Natural rubber, the original elastomer, still plays an important role among elastomers. Rubber is prepared from the milky juice (latex) obtained from *Hevea* rubber trees or other sources like gutta-percha and balata. Natural rubber is a linear polymer of isoprene hence it is also called as polyisoprene.



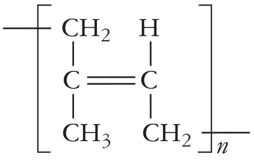
$$\underset{\text{Isoprene}}{n\mathrm{CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH{=}CH_2}} \longrightarrow \underset{\text{Polyisoprene}}{\mathrm{-[CH_2{-}\underset{\substack{|\\ CH_3}}{C}{=}CH{-}CH_2{-}]_n}}$$

Chemically, natural rubber from *Hevea* trees is *cis*-1,4 polyisoprene and that tapped from other sources (gutta-percha and balata) is the *trans* isomer of polyisoprene. The gutta-percha rubber is a hard and brittle polymer.



$$-\!\left[\begin{array}{cc} CH_2 & CH_2 \\ | & | \\ C & \!\!=\!\! C \\ | & | \\ CH_3 & H \end{array}\right]_n\!-$$

Natural rubber



$$-\!\left[\begin{array}{cc} CH_2 & H \\ | & | \\ C & \!\!=\!\! C \\ | & | \\ CH_3 & CH_2 \end{array}\right]_n\!-$$

Gutta-percha

Processing of Latex

Latex is obtained from rubber tree by making a cut in the bark and tapping. The milky emulsion is collected in a container and preserved by adding small amounts of ammonia. The tapping process continues for the entire lifespan of the tree. The emulsion contains 30–40% rubber dispersed in the solution, along with some proteins and resins. Latex concentrate is produced by centrifuge, concentrating the field latex tapped from rubber trees. The dry rubber content is subsequently increased to 60% or more.
Crude rubber is obtained by further processing of the latex by any one of the following steps:

1. **Coagulation:** Raw rubber can be coagulated by heating or addition of dilute acid (acetic or formic acid) solution or potassium alum. The coagulum is washed with water, dried and rolled into thick sheets which are dried further in smoke from burning wood. The crude rubber thus obtained is called *smoke rubber*. In another process, the coagulum is bleached and rolled into thin sheets and air-dried to obtain another form of crude rubber called *crepe rubber*. Both the forms are further processed to improve properties of crude rubber by techniques described in the following subsection.
2. **Direct precipitation:** Raw rubber can also be precipitated directly from the emulsion by mixing with compounding materials (discussed in the following subsection) and molded into required shape.

Processes for Improvement of Properties of Natural Rubber

Natural rubber's principal uses are automotive tyres, tyre tread and mechanical goods. Automotive applications are always compounded with carbon black to impart UV resistance and to increase mechanical properties. Latex concentrate is used for dipped goods, adhesives and latex thread.

Although NR is satisfactory for many applications, its use is limited by the fact that it is a natural crop produced only in tropical countries. The other drawbacks associated with its use are as follows:

1. It becomes hard and brittle at low temperatures and soft and sticky at high temperatures.
2. It has poor storage capacity (it develops bad odor on storage).
3. It has high water absorption capacity.
4. It is non-resistant to organic solvents, non-polar solvents and oxidizing agents.
5. It exhibits very weak tensile strength.
6. It has poor abrasion resistance.
7. It suffers permanent deformation because of the sliding of molecular chains over each other.
8. It is sensitive to oxidative degradation.

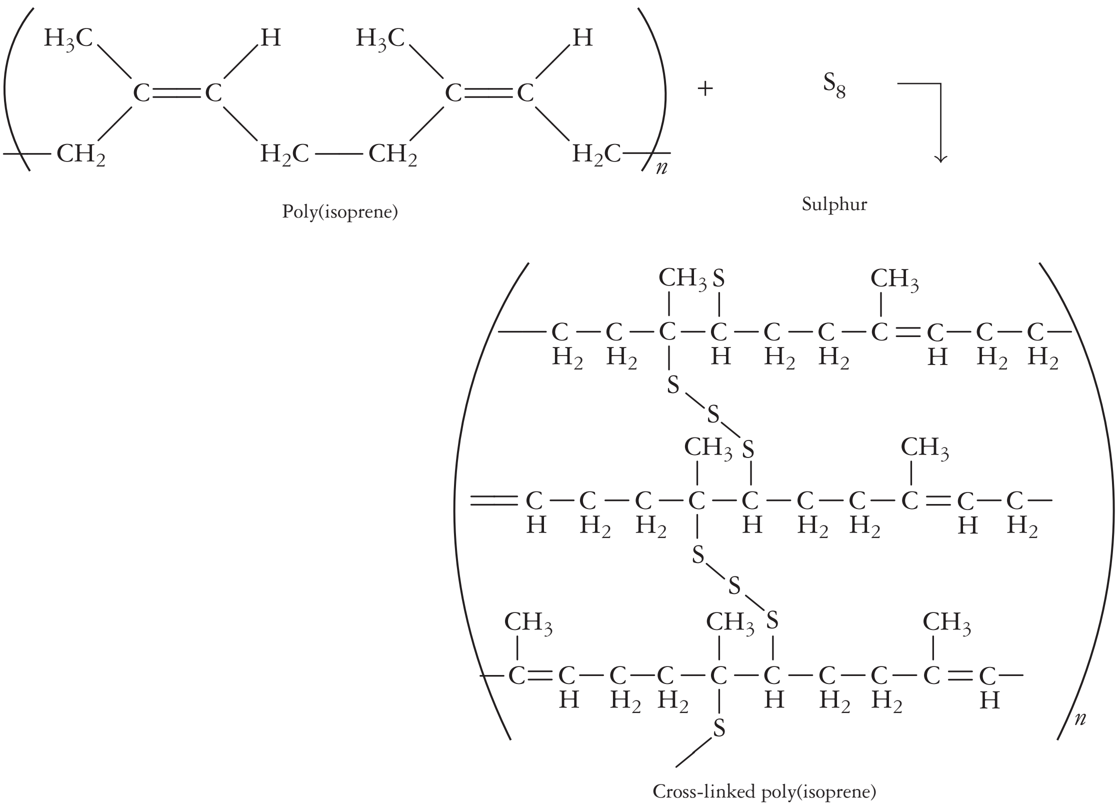
To overcome the drawbacks discussed above, natural rubber is subjected to processes such as vulcanization and compounding to improve its properties.

Vulcanization

The process of heating and mixing the crude rubber with sulphur to a definite temperature for a specific time is known as vulcanization. This process of curing natural rubber modifies it to become more durable with better mechanical properties. The sulphur combines chemically at the double bonds forming cross-links between different polymer chains. This cross-linking brings about stiffness in the rubber, and subsequently prevents intermolecular sliding of rubber polymer chains.

The extent of stiffness of vulcanized rubber depends upon the amount of the sulphur added. For example, a rubber tyre contains 3–5% sulphur, whereas a battery case made from rubber may contain as much as 30% of sulphur. This highly vulcanized rubber is called ebonite. Apart from sulphur, other vulcanizing agents are also used. These include hydrogen sulphide, sulphur monochloride, benzoyl chloride, etc.

There are a number of methods for sulphur vulcanization, with certain methods producing polysulphidic cross-linking and other methods producing more monosulphidic cross-links. The most economical method used for vulcanization of rubber in manufacture of tyres involves high temperature (170°C) and pressure conditions. Other methods use hot air vulcanization or microwave heated vulcanization.



Properties of vulcanized rubber:

1. It has good tensile strength and extensibility.
2. It has excellent resilience.
3. It possesses low water absorption capacity.
4. It has higher resistance to oxidation and to abrasion, wear and tear resistance.

5. It is resistant to organic solvents such as petrol, benzene, CCl_4 and fats and oils. However, it swells in these liquids.
6. It exhibits good electrical insulation property.
7. It has a wide useful temperature range from −40°C to 100°C.
8. It is very easy to tailor make the properties of vulcanized rubber for the specific needs.

Compounding

Compounding is mixing of the raw rubber (natural or synthetic) with other ingredients so as to impart the specific properties to the end product. The compounding of rubber involves the use of the following materials, depending on the end use of the product.

1. **Plasticizer:** These are often added to raw rubber to improve the flexibility and adhesion. Common plasticizers used are oils, paraffins, waxes, etc.
2. **Accelerators:** In order to speed up the vulcanization process, accelerators are added along with the sulphur. In addition, accelerators also improve the physical properties of the rubber. The most commonly used accelerators are aldehydes, amines, benzothiozole, etc.
3. **Fillers:** These are added to give strength and rigidity, and reduce cost of the rubber products. Carbon black powder is the most common reinforcing filler used for the manufacturing of motor car tyres. It is the cheapest and most effective filler. Other fillers such as zinc oxide, calcium carbonate and magnesium carbonate are also widely used.
4. **Antioxidants:** Natural rubber has a tendency to undergo degradation due to oxidation. Therefore, chemicals called antioxidants are added to prevent early deterioration on rubber by retarding oxidation. They also help to prevent rubber from becoming hard and brittle. Amines, phenols, β-napthols, etc., are commonly used antioxidants.
5. **Coloring agents:** These are added to give the desired color to the rubber products. For white colored rubber products, the pigments like zinc oxide, titanium dioxide are added; while for colored products, pigments like chromium oxide (green), ferric oxide (red) and lead chromate (yellow) are added.

Even by cross-linking, all the drawbacks of natural rubber cannot be overcome; therefore, synthetic rubbers have been developed.

Synthetic Rubbers

All the drawbacks associated with natural rubber cannot be overcome by the processing techniques discussed above. Therefore, synthetic rubbers have been developed for a wide range of applications with specific properties as per the use.

The advantages of synthetic rubbers over natural rubber are discussed as follows:

1. It is produced using monomers derived from petrochemical raw materials.
2. It is more economical than natural rubber.
3. It is superior to natural rubber in certain properties, such as tensile strength and abrasion resistance.
4. It can be tailor-made to the end properties and use.
5. Synthetic rubbers have low temperature flexibility and high temperature stability.

Concept Check

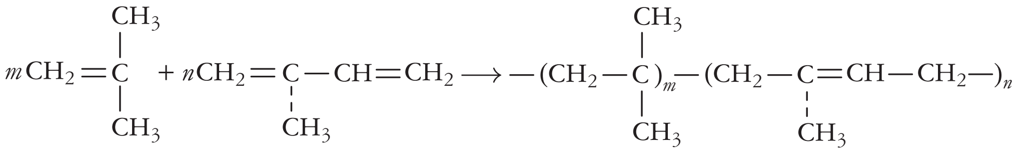
- Discuss the chemical structure of natural rubber obtained from different sources.
- What are the steps involved in the processing of latex to obtain natural rubber?

- What is vulcanization? How does it improve the properties of raw rubber?
- Discuss the various compounding agents used to impart specific properties to raw rubber.
- What are the advantages of synthetic rubber over raw rubber?
- What are the limitations of raw rubber?

10.11 Some Important Synthetic Rubbers

Butyl Rubber (GR-I Rubber)

Butyl rubber is a copolymer of isobutylene and isoprene. It is manufactured by mixing 95% isobutylene with 5% of isoprene in the presence of anhydrous $AlCl_3$ dissolved in methyl chloride as catalyst at −95°C.



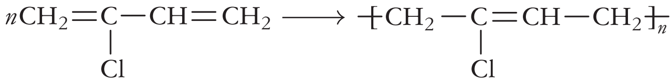
$$m\,CH_2{=}\underset{CH_3}{\overset{CH_3}{C}} + n\,CH_2{=}\underset{CH_3}{C}-CH{=}CH_2 \longrightarrow -(CH_2-\underset{CH_3}{\overset{CH_3}{C}})_m-(CH_2-\underset{CH_3}{C}{=}CH-CH_2-)_n$$

Isobutylene Isoprene Butyl rubber

Applications: It is used for making inner tubes for tyres, conveyor belts and tank linings. It is also used for insulating high-voltage wires and cables.

Polychloroprene (Neoprene or GR-M Rubber)

Polychloroprene is prepared by emulsion polymerization of chloroprene in the presence of persulphate as initiator. Neoprene is the DuPont Chemical trade name for a family of synthetic rubbers based on *polychloroprene*.



$$n\,CH_2{=}\underset{Cl}{C}-CH{=}CH_2 \longrightarrow \left[CH_2-\underset{Cl}{C}{=}CH-CH_2\right]_n$$

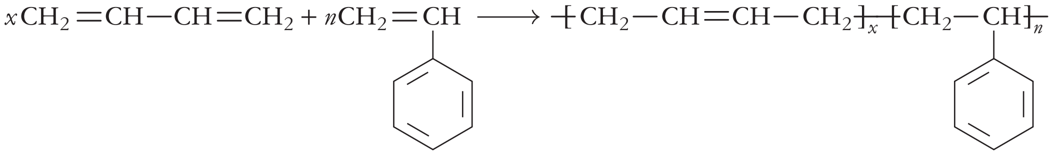
Chloroprene Polychloroprene

Vulcanization of neoprene is carried out using ZnO or MgO, because process with sulphur is extremely slow.

Applications: It is used for manufacture of conveyor belts, car fan belts, gaskets, hoses, mouse pads, shoe heels. It is also used for corrosion resistance coatings, lining material in reaction vessels and tubes for carrying oils and chemicals. It also finds use as adhesive in tapes and highway joints, and in gloves.

Styrene–Butadiene Rubber (SBR) (Buna-S or GR-S Rubber)

Styrene–butadiene rubber is prepared by the copolymerization of butadiene (75%) and styrene (25%) in an emulsion polymerization at 50°C in the presence of catalysts such as cumene hydroperoxide. SBR is also known as Buna-S.



Butadiene Styrene Styrene butadiene rubber (SBR)

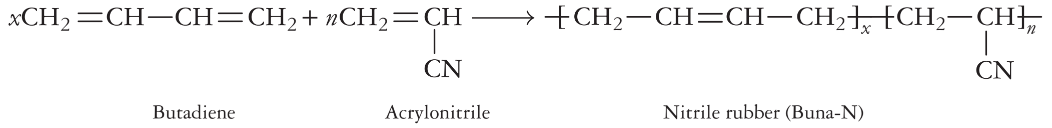
Properties:

1. It has high abrasion resistance and load-bearing capacity.
2. It has low oxidation resistance and swells in oil and solvents, like natural rubber.
3. SBR also vulcanizes to produce cold rubber, which has greater tensile strength and abrasion resistance.

Applications: SBR is used in motor tyres, shoes soles, footwear components, insulation of wires and cables, carpet backing, gaskets and adhesives.

Nitrile Rubber (NBR) (Buna-N or GR-A Rubber)

Nitrile rubber is a copolymer of acrylonitrile and butadiene. It is prepared by the copolymerization of acrylonitrile and butadiene by emulsion polymerization.



$$x\mathrm{CH_2{=}CH{-}CH{=}CH_2} + n\mathrm{CH_2{=}}\underset{\overset{|}{\mathrm{CN}}}{\mathrm{CH}} \longrightarrow \left[\mathrm{CH_2{-}CH{=}CH{-}CH_2}\right]_x \left[\mathrm{CH_2{-}}\underset{\overset{|}{\mathrm{CN}}}{\mathrm{CH}}\right]_n$$

Properties:

1. It has low swelling and low solubility.
2. It has good tensile strength and abrasion resistance even after immersion in oil.
3. It also possesses good heat resistance.

Applications: Nitrile rubber is used in fuel tanks, gasoline hoses, as an adhesive and in the form of latex for impregnating paper, leather and textiles.

Polysulphide Rubber

Polysulphide rubber is prepared by the reaction between sodium polysulphide and ethylene dichloride. It is also known as thiokol. These thiokols are elastomers in which sulphur forms a part of the polymer backbone.

$$\mathrm{Cl{-}CH_2{-}CH_2{-}Cl} + \mathrm{Na{-}S}_x\mathrm{{-}Na}$$

Ethylene dichloride

$$\downarrow$$

$$\left[\mathrm{CH_2{-}CH_2{-}S}_x\right]_n + \mathrm{NaCl}$$

Polysulphide rubber

Properties:

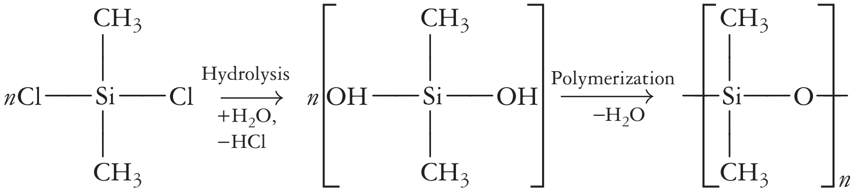
1. It has extremely good resistance to mineral oils, oxygen, ozone and sunlight.
2. It is also impermeable to gases.
3. Since it does not contain unsaturation, it cannot be vulcanized and hence has poor abrasion resistance and strength.
4. Its limitations, compared with nitrile rubber, are relatively poor tensile strength, rebound, abrasion resistance, high creep under strain and odor.

Applications: Polysulphide rubbers are mainly used to make sealants, balloons, protective coatings on metals, binders in gaskets, fabric coatings and gasoline hoses. It is used to provide water and solvent resistance to leather.

It can form excellent fuel material and upon mixing with inorganic oxidizers, they become solid propellants for rockets.

Silicone Rubber

Hydrolysis of chlorosilane gives dimethyl silicon hydroxide intermediate (unstable), which undergoes polymerization to give dimethyl silicone polymer (silicone rubber). Silicone rubber can be cross-linked between two adjacent chains by using organic peroxides.



$$n\mathrm{Cl}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{Cl}\xrightarrow[+\mathrm{H_2O},\ -\mathrm{HCl}]{\text{Hydrolysis}} n\left[\mathrm{OH}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{OH}\right]\xrightarrow[-\mathrm{H_2O}]{\text{Polymerization}}\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]_n$$

Applications:

1. As a sealing material in searchlights and in aircraft engines.
2. For insulating the electrical wiring in ships.
3. As adhesive in electronic industry.
4. For making boots for use at low temperature.
5. For manufacture of tyres for fighter aircrafts.
6. In making artificial heart valves, transfusion tubings and padding for plastic surgery.
7. In making insulation for washing machines and electric blankets for iron board covers.

Concept Check

- What are the chemical reactions involved in the preparation of butyl rubber and polychloroprene rubber?
- Discuss the preparation and properties of styrene–butadiene rubber. List two of its important uses.
- What is thiokol? How is it prepared? What are its limitations compared to nitrile rubber?
- How does butyl rubber differ from Buna-S?
- What are silicone rubbers? Mention their important applications.

10.12 Fibers

A fiber is generally defined as a flexible, macroscopically homogeneous body having a high length-to-width ratio and a small cross-section. Fibers can be incorporated as a whole or parts of materials to obtain products of various forms, and performance properties for a wide-range of applications. The unique combination of characteristics of constituting fibers determine not only how fibers can be put together and made into products, but also the performance of these products.

Physical Properties

Thermal, optical, surface and electrical properties are among the important physical properties of fibers. Since fibers are frequently subjected to elevated temperatures, it is necessary that they have high melting or degradation points. It is also necessary that other fiber properties are relatively constant as a function of temperature over a useful temperature range.

Luster and color are two optical properties that relate to a textile fiber's aesthetic quality and consumer acceptance. These fibers should be optically opaque, so their refractive indexes should be significantly different from that of their most common environments, namely, air and water.

Textile fibers are always used in aggregates of a large number of single fibers that are caused to interact with each other through their surfaces. The surface characteristics of fibers, therefore, are of singular importance. Inter-fiber friction and geometric roughness or rugosity are two surface properties that relate directly to processibility and product performance.

Electrical properties also affect the utility of the fiber. In view of their chemical structure, most textile fibers are non-conducting and can be classified as insulators because of their high resistivity. Fibers are subjected to static electrification, and some means of discharging them needs to be employed in high-speed manufacturing processes and in certain end-uses. In fibers that absorb water vapor from the atmosphere, water molecules increase electric conductivity and dissipate the electric charges. However, static electrification remains a problem with hydrophobic fibers. This is overcome by blending such fibers with electrically conducting fibers, to reduce the static charge generated during textile processing and end use.

Types of Fibers

Fibers are traditionally classified according to their origin as follows:

1. **Naturally occurring fibers:** These can be further classified as fibers of the following origins:
    - Plant origin based on cellulose, for example, cotton, flax, hemp, jute and ramie.
    - Animal origin based on proteins, for example, silk, wool, mohair, vicuna and other animal hairs.
    - Mineral origin, for example, asbestos.
2. **Regenerated fibers (semi-synthetic):** These are based on natural cellulose and proteins and include
    - Rayon containing regenerated cellulose.
    - Acetate containing partially acetylated cellulose derivative.
    - Triacetate containing fully acetylated cellulose derivative.
    - Azlon containing regenerated protein.
3. **Synthetic fibers:** These are based on synthesized organic polymers. Some common examples include
    - Acrylic (polyacrylonitrile).
    - Aramid (aromatic polyamide).
    - Nylon (aliphatic polyamide).
    - Olefin (polyolefin).
    - Polyester (polyester of an aromatic dicarboxylic acid and a dihydric alcohol).
    - Spandex (segmented polyurethane).
    - Vinyon (polyvinyl chloride).
    - Vinal (or vinylon) (polyvinyl alcohol).
    - Specialty fibers (polyphenylene sulphide and polyetheretherketone).
4. **Inorganic fibers:** These include
    - Carbon/graphite fibers.
    - Glass, metallic or ceramic fibers.

Spinning Processes

For the spinning of fibers, the molten polymer (in the case of dry or wet spinning, the spin dope) is first pumped through a filter, which removes any tiny particle that can be trapped in the tiny spinneret holes. The polymer is then forced through these tiny holes to form continuous strands of polymer filaments, or synthetic fibers. Cooling gases reduce the temperature of the filaments so that they solidify, and an initial drive roll controls the initial take-up speed. The fiber may undergo subsequent heating and stretching to impart additional molecular orientation. Finally, the fiber is taken up onto bobbins at a constant speed, with a special tension control device to control the rate of rotation in order to maintain constant yarn speed (Figure 6).

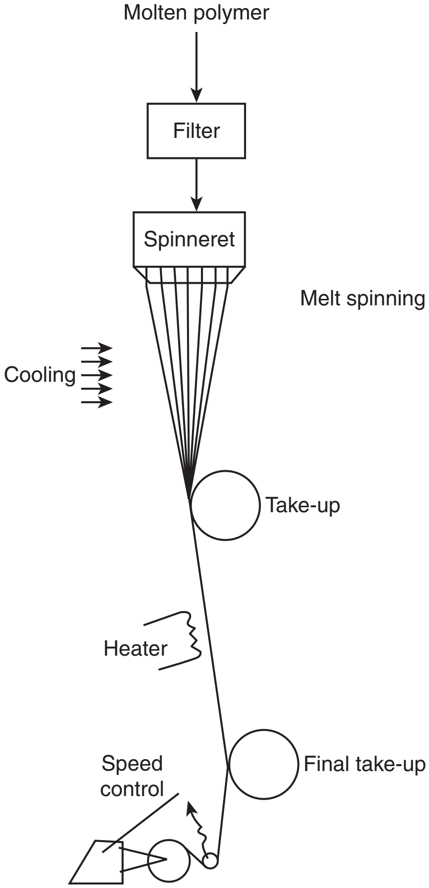


Figure 6 Schematic representation of melt spinning process.

Concept Check

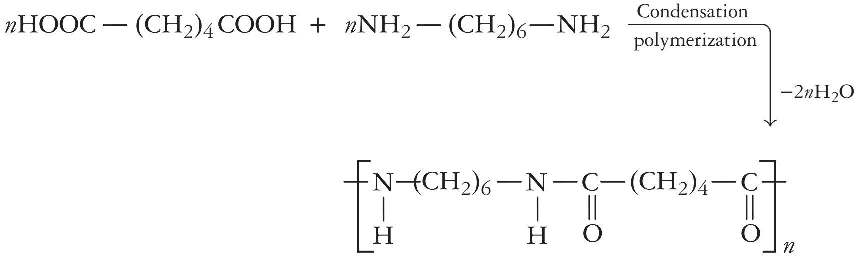
- What are fibers? How are naturally occurring fibers classified?
- What are the different types of fibers? Give an example of each kind.
- Describe the melt spinning process for fibers.

10.13 Some Important Synthetic and Semi-synthetic Fibers

Nylons (Polyamides)

Nylons are condensation polymers that belong to the class of polyamides. The important synthetic fibers of this category are nylon-6 and nylon-6,6. There two general approaches to synthesis of nylon by polymerization.

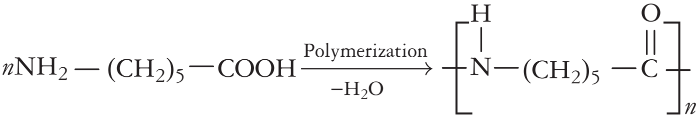
1. This approach involves combining molecules with an acid (COOH) group on each end (dicarboxylic acids) with molecules that contain amine (NH_2) groups on each end (diamines). Nylon-6,6 is prepared by this method. The first number indicates the number of carbon atoms present in diamine and the second number indicates the number of carbon atoms in dicarboxylic acid.
   The condensation copolymerization of adipic acid with hexamethylene diamine in equimolar ratio yields nylon-6,6 (polyhexamethylene adipamide).



$$n\mathrm{HOOC-(CH_2)_4COOH} + n\mathrm{NH_2-(CH_2)_6-NH_2} \xrightarrow[\text{polymerization}]{\text{Condensation}} \xrightarrow{-2n\mathrm{H_2O}} \left[\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}} - (\mathrm{CH_2})_6 - \underset{\mathrm{H}}{\underset{|}{\mathrm{N}}} - \underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}} - (\mathrm{CH_2})_4 - \underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}} \right]_n$$

Nylon-6,6

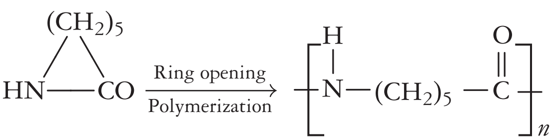
2. In this approach, a compound with acid group at one end and an amine at the other end is polymerized to form a chain with repeating units of the type (–NH–$[CH_2]_n$–CO–). Nylon-6 is prepared by this method. It can be prepared by:
   - Self-condensation of ε-aminocaproic acid:



$$n\mathrm{NH_2-(CH_2)_5-COOH} \xrightarrow[-\mathrm{H_2O}]{\text{Polymerization}} \left[\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}} - (\mathrm{CH_2})_5 - \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} \right]_n$$

Nylon-6

   - Ring-opening polymerization of a caprolactum:



Nylon-6

Properties

1. Nylon fibers are linear structures in which the molecular chains are arranged parallel to each other and held together by hydrogen bonding. The strong intermolecular hydrogen bonding makes the structure of these fibers crystalline and imparts them high strength, elasticity and melting point.
2. They are chemically stable and resistant to abrasion.

3. The yarn is smooth, long-lasting and can be spun into fabric.
4. The fabric is tough, lustrous, moisture resistant, easy to dye, retains color and can be set by heat or steam.

Applications

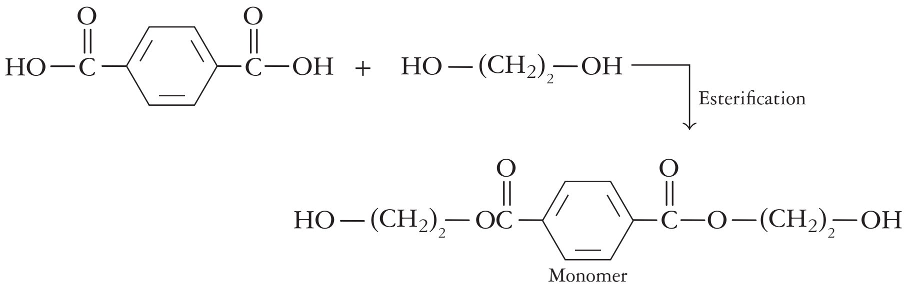
Nylons find extensive use because of their unique thermo-mechanical properties.

1. Nylon is used for making sports gear, fishing lines and other recreational equipment.
2. It is used for making combs and bristles of the brushes.
3. As engineering application, it is used for making gears, bearings, bushes, etc.
4. It is used for jacketing electrical equipment to provide insulation and resistance to abrasion.
5. Nylon-6 is mainly used for making cords for tyres.
6. Nylon-6,6 fibers are used for making fabric for clothing, socks, sportswear, carpets, etc.

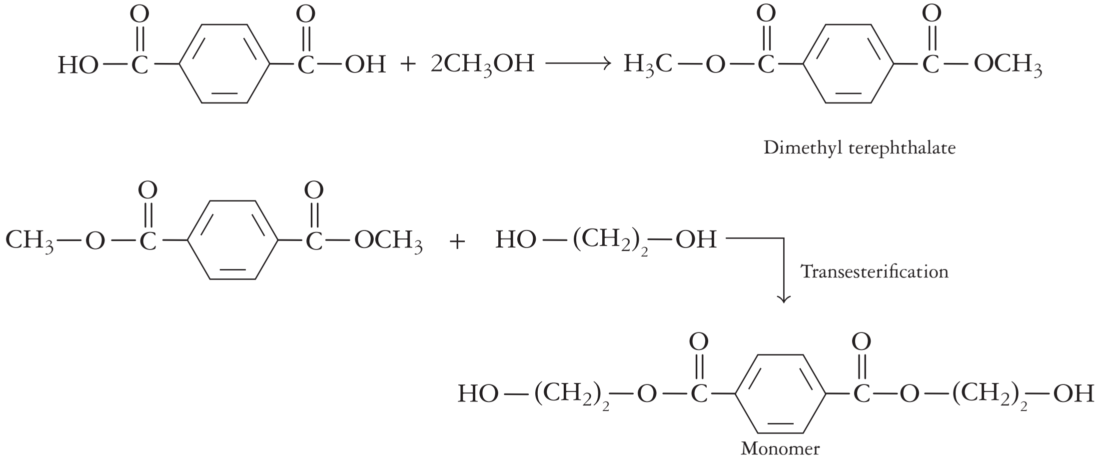
Polyethylene Terephthalate (Polyester)

Polyethylene terephthalate (PET) is a saturated thermoplastic polyester that can be extruded into synthetic fibers or films. It is commonly known as dacron. The monomer *bis*-β-hydroxyterephthalate can be synthesized by the following two pathways:

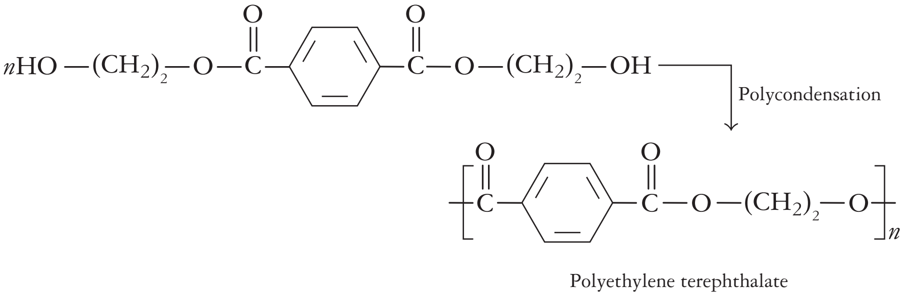
1. Esterification reaction between terephthalic acid and ethylene glycol with water formed as a byproduct.



2. Transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol formed as a byproduct.



Immediately after esterification/transesterification, the monomer formed undergoes polycondensation to yield the polymer PET with ethylene glycol formed as the byproduct.



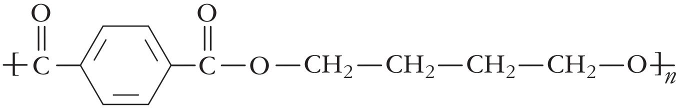
Properties

1. PET can exist both in amorphous (transparent) and semi-crystalline (white) form.
2. It has high mechanical strength and dimension stability and is stable over temperature range of −40°C to 100°C.
3. It shows creep and abrasion resistance and good electrical insulating properties.
4. It shows low water absorption; and at room temperature, it is resistant to water, dilute acids, salts, aromatic and aliphatic hydrocarbons and alcohols.

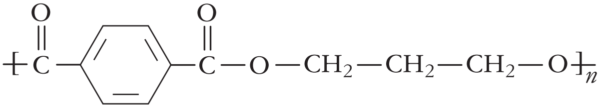
Applications

1. It is used for making video and audio tapes.
2. Its most common use is in making clear bottles for foods and beverages.
3. It is used to make films for shrink packaging.
4. As an electrical insulator, it is used for making molds for electrical appliances.
5. The synthetic fibers can be woven to make upholstery, artificial grass, etc.
6. The fiber may be blended with wool and other natural fibers.
7. The films may be combined with paper or other polymeric films to form multilayer material.
8. It can be used to produce injection molded articles, such as switches, valves, etc.

Apart from PET, two other polyester fibers that are commonly used are poly (butylene terephthalate) (PBT) and poly (trimethylene terephthalate). They find applications similar to that of PET but may be put to specific uses because of their properties. For example, PBT finds wider use in injection molding products.



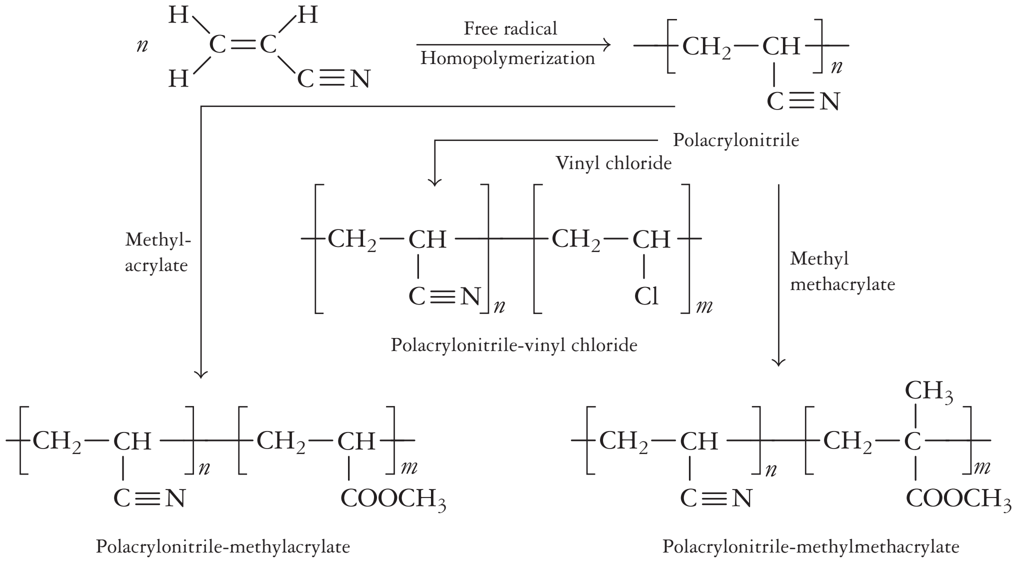
Poly(butylene terephthalate)



Poly(trimethylene terephthalate)

Acrylic Fibers (Polyacrylonitriles)

Polacrylonitriles (PAN) refer to class of polymers which are homopolymers or copolymers formed with acrylonitrile as the main component. Copolymerization is usually carried out with vinyl chloride, methyl methacrylate, butadiene or styrene to obtain different PANs.



Properties

1. The homopolymer has good insulation properties, high anti-aging strength, and reasonable chemical stability. It shows color fastness when exposed to light.
2. The copolymer with styrene has good mechanical strength.
3. The copolymer with vinyl chloride is flame retardant.

Applications

1. Fiber obtained by homopolymerization of acrylonitrile is used for making hot gas filtration systems, outdoor awnings and sails for yachts. These fibers also find use in fiber reinforced concrete.
2. Fibers obtained by copolymerization with methyl acrylate and methylmethacrylate are used to make knitted clothing, like socks and sweaters, as well as outdoor products such as awnings, etc. All materials labeled as "acrylic" generally refer to these copolymers.
3. Copolymers such as styrene-acrylonitrile and styrene-acrylonitrile-butadiene are used as plastics.

Concept Check

- What are nylons? Explain the significance of numbers in nylon-6,6 and nylon-6.
- How is nylon-6 prepared? How does the approach of its synthesis differ from the preparation of nylon-6,6?

- Discuss the important applications of nylons in relation to their thermo-mechanical properties.
- Discuss the two pathways used for synthesis of PET. Why is it used extensively for making bottles/containers for food and beverages?
- What are acrylic fibers? Give their structures and important properties.

10.14 Conducting Polymers

Until 1960, all organic polymers were used in electrical, electronic and other applications as insulators, taking advantage of their excellent insulation properties (high resistance to the flow of current).

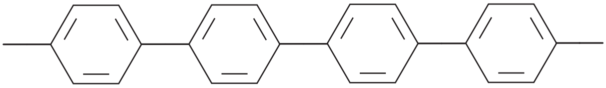
The idea that polymers can also conduct electricity as good as metals was discovered accidentally at the plastic research laboratory of BASF, Germany in 1977. A chemist by the name Shirakawa accidentally added a catalyst 1000 times more than the required amount during the polymerization of acetylene, which resulted in a conducting polyacetylene. Organic polymers having electrical conductance of the order of conductors are now called conducting polymers. These can be classified as extrinsically and intrinsically conducting polymers.

Extrinsically conducting polymers are prepared by mixing conducting fillers like metal fibers, metal oxides, carbon black with insulating polymers. These are also called *conductive element filled polymers*. In this type of conducting polymers, insulating polymer forms the continuous phase and the added fillers form the conducting network. A minimum concentration of conducting filler has to be added so that the polymer starts conducting. The conductivity in this type of polymers is not due to the matrix polymer but due to the conducting fillers which are added. However, in case of intrinsically conducting polymers, conductivity is due to the organic polymers themselves. They conduct electricity when doped with oxidizing or reducing agents or protonic acids.

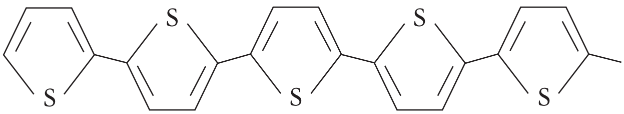
Conducting Polymers with Conjugated π-Electrons

Organic polymers with highly delocalized π-electron system having electrical conductance of the order of conductors are called inherently or intrinsically conducting polymers, or synthetic metals. The basic requirement for organic polymer to be inherently conducting is the formation of continuous conjugation (alternative single and double bonds) through the polymer chain.
The following are examples for intrinsically conducting polymers:

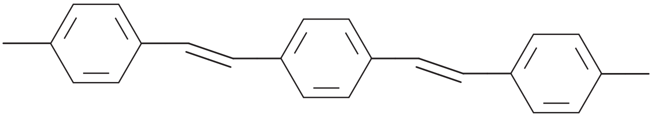
1. Poly (*p*-phenylene)



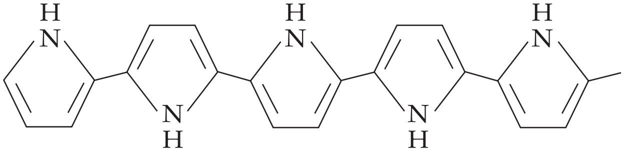
2. Polythiophene



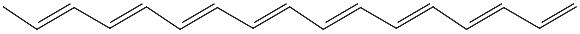
3. Poly(*p*-phenylene vinylene)



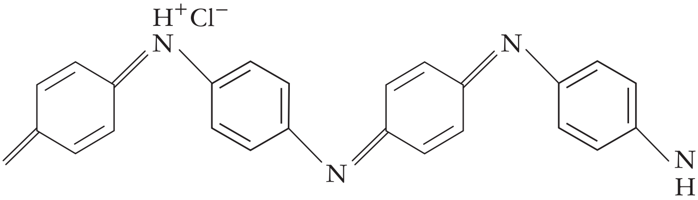
4. Polypyrrole



5. *Trans*-polyacetylene



6. Polyaniline

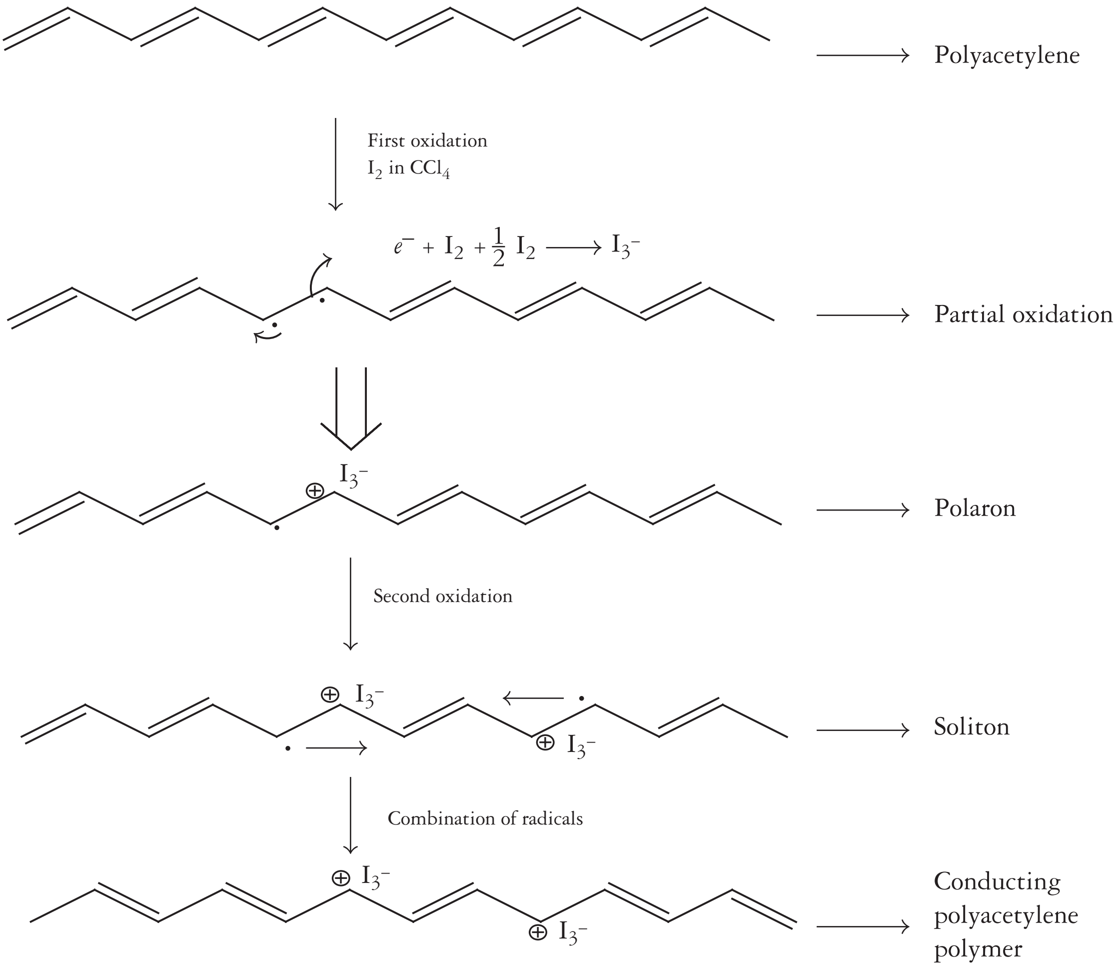


These conjugated organic polymers in their pure state are either insulators or semiconductors. The π-electrons are normally localized and do not take part in conductivity. But these electrons delocalize on doping and conduct electricity. The dopant may be oxidizing or reducing agent, and protonic acids. Accordingly, they are called *p*-doping or *n*-doping and *H*-doping polymers. In practice, most organic conductors are doped oxidatively to give *p*-type materials. The redox doping of organic conductors is similar to the doping of silicon semiconductors with electron-rich phosphorus or electron-poor boron atoms to create *n*-type and *p*-type semiconductors, respectively.

Polyacetylene

Polyacetylene consists of chains of hundreds to thousands of carbon atoms linked by alternating single and double bonds. Conductivity of pure polyacetylene is about 4.4×10^{-5} S/cm. Upon doping with oxidizing agents like iodine, the conductivity increases to about 400 S/cm.

When the oxidative dopant such as iodine is added, it takes away an electron from the π-backbone of the polyacetylene chain and creates a positive center (hole) on one of the carbons. The other π-electron resides on the other carbon making it a radical. The radical ion formed is called polaron. A dipolaron (soliton) is formed on further oxidation. Then these radicals migrate and combine to establish a backbone double bond. As the two electrons are removed, the chain will have two positive centers (holes). The chain as a whole is neutral, but holes are mobile and when a potential is applied they migrate from one carbon to another and account for conductivity. This is depicted by the sequence of reactions as follows:



When a π-bond is formed, valence band (VB) and conduction band (CB) are created. Before doping, there is sufficient energy gap between VB and CB, so the electrons remain in VB and the polymer acts as an insulator. Upon doping, polarons and solitons are formed which results in the creation of new localized electronic states that fill the energy gap between VB and CB. When sufficient solitons are formed, a new mid-gap energy band is created which overlaps with the valence and conduction bands allowing electrons to flow (Figure 7). The charged solitons are thus responsible for making polyacetylene a conductor.

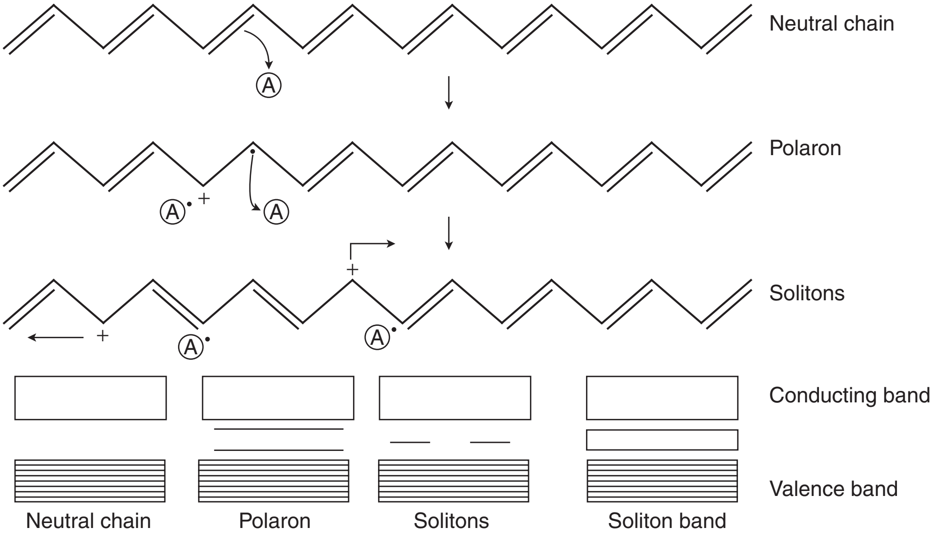
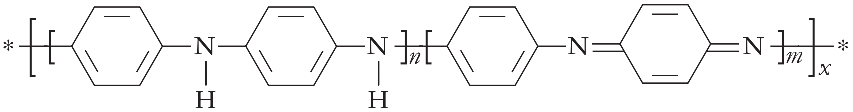


Figure 7 Formation of new mid-gap energy band between VB and CB.

Polyaniline

Polyaniline is a typical phenylene-based polymer having a flexible –NH– group flanked on either side by a phenylene ring. The various physicochemical properties of polyaniline are due to the presence of the –NH– group. It is represented as follows:



Polyaniline exists in a variety of forms (oxidation states) that differ in their conductivity. The most common form, that is, green protonated emeraldine has conductivity of the order of semiconductor level (1 S/cm). This is higher than that of ordinary polymers ($<10^{-9}$ S cm^{-1}) but lower than that of metals ($>10^4$ S/cm).

The emeraldine form of polyaniline can also be electrochemically oxidized or reduced in aqueous acid resulting in pernigraniline (PS) and leuco-emeraldine (LS) salts, respectively, as shown in Figure 8. This process is known as protonic acid doping. The redox reaction occurs with the motion of protons and electrons in strong acid ($\text{pH} < 3$). The addition of protons and electrons to nitrogen is observed during the reduction; this leads to ring changes from phenyl to quinoid structure upon oxidation and vice versa during reduction). The generation of these charged carriers is responsible for the conductivity of the polymer. Protonated polyaniline converts into a non-conducting blue emeraldine base when treated with a base.

Different oxidation states of polyaniline can also be generated by doping with oxidants such as iodine. The conductivity of the resulting form of polyaniline is, however, lower than that obtained by protonic acid doping.

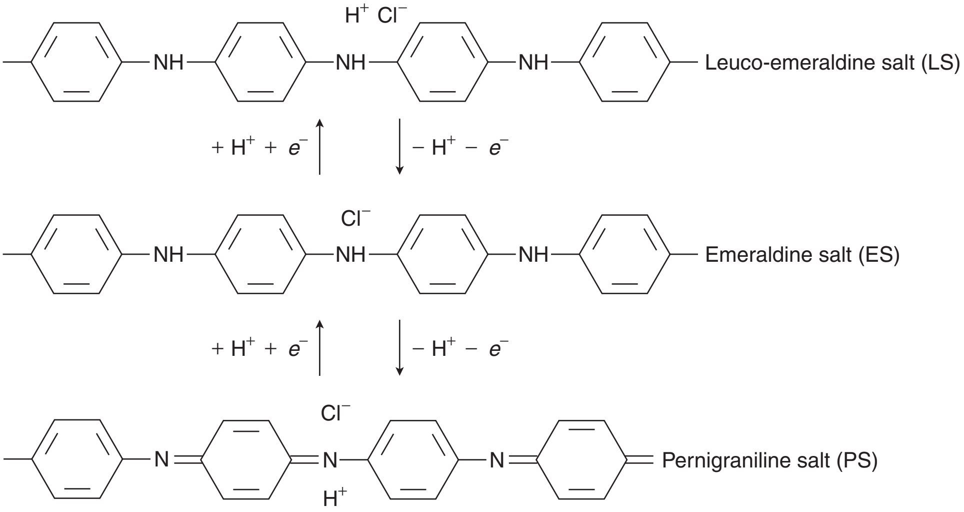


Figure 8 Formation of pernigraniline (PS) and leuco-emeraldine (LS).

Applications of Conducting Polymers

Conducting polymers find use in the following:

1. They are used in antistatic materials.
2. They are used as electrode materials for rechargeable batteries.
3. They are used in light-emitting diodes.
4. They are used in ion commercial displays.
5. They are used as conductive track on printed circuit boards (polyaniline).
6. They are used as a resist for lithography (emeraldine base).
7. They are used in information storage devices.
8. They are used as humidity sensors, gas sensors, radiation sensors.
9. They are used in electrochromic display windows.
10. They are used in fuel cells as electrocatalytic materials.
11. They are used as membrane for gas separation.

Concept Check

- What are conducting polymers? Discuss their classification into intrinsic and extrinsic polymers.
- Explain the conductivity of polymers with conjugated π-electron systems. How is this conductivity enhanced by doping?
- Explain the mechanism of conduction in polyacetylene.
- Discuss the different oxidation states of polyaniline and their conductivity.

Key Terms

Monomers
Polymers
Polymerization
Homopolymer
Copolymer
Random, block, graft copolymerization
Functionality
Degree of polymerization
Linear, branched, cross-linked
Natural, synthetic polymers
Crystalline polymer
Isotactic, syndiotactic, atactic
Addition, condensation polymers
Elastomers
Resins
Thermoplastic and thermosetting
Free radical polymerization
Ionic polymerization
Coordination polymerization
Molecular weight of polymers
Glass transition temperature (T_g)
Polymethyl methacrylate Polyurethanes
Phenol–formaldehyde resins
Spinneret
Bakelite
Amino resins
Silicone resins
Natural rubber
Gutta-percha
Vulcanization
Ebonite
Buna-N, Buna-S
Polysulphide Rubber
Silicone Rubber
Regenerated fibers
Nylon
Polyacrylonitriles
Novolac and Resol
Conducting polymers

Objective-Type Questions

Multiple-Choice Questions

1. Which of the following can be used as monomers for polymerization?
   a. NH_3
   b. CH_3CH_2COOH
   c. $HOCH_2CH_2OH$
   d. All of the above.
2. Which among the following is trifunctional?
   a. Ethylene glycol
   b. Glycine
   c. Phenol
   d. Vinyl chloride
3. Polymer that softens on heating and stiffens on cooling is called
   a. thermoset.
   b. thermoplastic.
   c. elastomer.
   d. rubber.
4. Which of the following may not be used as criteria for classification of polymers?
   a. Number of monomers
   b. Structure/shape
   c. Thermal behavior
   d. None of the above.
5. Polymer with low degree of polymerization is known as
   a. high polymer.
   b. oligo polymer.
   c. macromolecule.
   d. copolymer.
6. The compound that can be used as initiator in addition polymerization is
   a. potassium dichromate.
   b. potassium sulphate.
   c. benzoyl peroxide.
   d. Any of the above.

7. Formation of free radicals from initiators in addition polymerization is
   a. exothermic process.
   b. endothermic process.
   c. depends on the compound used.
   d. cannot be predicted.
8. The species responsible for propagation of polymerization reaction of ethylene using benzoyl peroxide as initiator is
   a. cation.
   b. anion.
   c. free radical.
   d. any of the above.
9. An example of chain-growth polymer is
   a. nylon-6,6.
   b. bakelite.
   c. terylene.
   d. teflon.
10. An example of step-growth polymer is
   a. teflon.
   b. PVC.
   c. polybutadiene.
   d. bakelite.
11. Which of the following polymers is formed by condensation polymerization?
   a. Polyethylene terephthalate
   b. Polyethylene
   c. Polystyrene
   d. Polypropylene
12. Which of the following is a copolymer?
   a. Polythene
   b. Polyurethane
   c. Teflon
   d. Plexiglass
13. Which one of the following is a homopolymer?
   a. Buna-S
   b. Styrene acrylonitrile
   c. Polyvinyl chloride
   d. Buna-N
14. Which of the following has the largest molecular mass?
   a. Monomer
   b. Dimer
   c. Oligomer
   d. Polymer
15. With increase in molecular mass of the polymer, its glass transition temperature (T_g)
   a. increases.
   b. decreases.
   c. increases to a limit and remains constant.
   d. decreases to a limit and then remains constant.
16. A polymer with higher T_g value is
   a. PVC.
   b. polyethylene.
   c. polypropylene.
   d. polystyrene.
17. Glass transition temperature of polyethylene adipate compared to polyethylene terephthalate would be
   a. lower.
   b. higher.
   c. same.
   d. cannot be predicted.
18. Chemical resistance of a polymer decreases with
   a. increase in crystallinity.
   b. increase in cross-linking.
   c. increase in molecular mass.
   d. none of the above.
19. The property desirable for a polymer to exhibit elastomeric property is that
   a. it should have flexible chains with strong intermolecular forces.
   b. it should have rigid chains with strong intermolecular forces.
   c. it should have flexible chains with weak intermolecular forces.
   d. it should have rigid chains with weak intermolecular forces.
20. The polymer likely to be attacked easily by acids and alkali is
   a. polypropylene.
   b. polystyrene.

c. polyvinyl chloride.
d. polyester.

21. Which of the following polymers are hard?
a. Linear
b. Branched chain
c. Cross-linked
d. Thermoplastic

22. Which of the following properties does not influence the glass transition temperature?
a. Chemical resistivity
b. Molecular weight
c. Crystallinity
d. Presence of side group

23. The monomer tetrafluroethylene can be used for the preparation of
a. PMMA.
b. polyurethane.
c. teflon.
d. polyethylene.

24. The polymer used in making gaskets and filters in chemical industry is
a. polytetrafluoroethylene.
b. polymethylmethacrylic acid.
c. polyethylene.
d. polystyrene.

25. Polymer used in making laser disks and rear lights in cars is
a. polytetrafluoroethylene.
b. polymethylmethacrylate.
c. polyethylene.
d. polystyrene.

26. Polymer obtained from reaction between diisocyanates and dihydric alcohols is
a. polytetrafluoroethylene.
b. polymethylmethacrylic acid.
c. polyurethane.
d. epoxy resins.

27. Phenol–formaldehyde resin is commercially called
a. PVC.
b. bakelite.
c. elastomer.
d. nylon.

28. Epoxy resins are obtained from
a. bisphenol A and formaldehyde.
b. phenol and formaldehyde.
c. bisphenol A and epichlorohydrin.
d. bisphenol A and alkyl diisocyanates.

29. Copolymer of isoprene and isobutylene is known as
a. butyl rubber.
b. Buna-S.
c. PTFE.
d. polyurethane.

30. Low-density polyethene is obtained by using
a. anionic catalyst.
b. free radical indicator.
c. Ziegler–Natta catalyst.
d. cationic catalyst.

31. A linear polymer used mostly for forming textile fibers is
a. PVC.
b. nylon.
c. bakelite.
d. neoprene.

32. Phenol–formaldehyde is an example of
a. thermoelastic polymers.
b. thermoplastic polymers.
c. thermosetting polymers.
d. thermite polymers.

33. Which type of intermolecular forces are present in nylon-6,6?
a. van der Waals forces
b. Hydrogen bonding
c. Dipole–dipole interaction
d. None of the above

34. Which one of the following is a thermosetting polymer?
a. Polyvinyl chloride
b. Polystyrene
c. Polyethylene
d. Polyester

35. Nylon-6,6 is a
a. polyester fiber.
b. polyamide fiber.
c. polyglycol derivative.
d. polyacrylate fiber.

36. The fiber obtained by reaction of hexamethylenediamine and adipic acid is
    a. nylon-6,6.
    b. nylon-6.
    c. terylene.
    d. orlon.

37. The example of a thermosetting polymer is
    a. PMMA.
    b. PVA.
    c. teflon.
    d. dacron.

38. Sulphur is used particularly in the
    a. manufacture of Buna-S.
    b. compounding of plastics.
    c. corrosion control.
    d. vulcanization of raw rubber.

39. Highly vulcanized rubber is called
    a. ebonite.
    b. bakelite.
    c. hematite.
    d. magnetite.

40. The polymer used in making inner tubes of tyres is
    a. neoprene rubber.
    b. butyl rubber.
    c. styrene butadiene rubber.
    d. natural rubber.

41. Which one of the following is an elastomer?
    a. PVC
    b. Bakelite
    c. Natural rubber
    d. Nylon

42. Raw rubber on vulcanization becomes
    a. plastic.
    b. tacky.
    c. soft.
    d. less elastic.

43. Which of the following rubbers is used for the manufacture of rubber tyres?
    a. Styrene rubber
    b. Nitrile rubber
    c. Neoprene rubber
    d. Butyl rubber

44. Which of the following properties is reduced on vulcanization of rubber?
    a. Tensile strength
    b. Elasticity
    c. Insulation property
    d. Resilience

45. Which one of the following is not synthetic rubber?
    a. Neoprene
    b. Polyisobutylene
    c. Polyisoprene
    d. Polyurethane

46. Which of the following has cross-links?
    a. Urea–formaldehyde resin
    b. Vulcanized rubber
    c. Buna-S
    d. Both a and b

47. Gutta-percha is
    a. trans-polymer of isoprene.
    b. *cis*-polymer of isoprene.
    c. Buna-S.
    d. Buna-N.

48. Styrene–butadiene rubber (SBR) is the example of
    a. addition polymerization.
    b. condensation polymerization.
    c. copolymerization.
    d. natural rubber.

49. The chemical formula of natural rubber is
    a. $(C_2H_8)_n$
    b. $(C_2H_8)_2$
    c. $(C_5H_8)_n$
    d. $(C_5H_8)_8$

50. Which of the following is the requirement for conductivity in polymers?
    a. Linear structure
    b. Presence of oxidizing or reducing agent
    c. Conjugation
    d. All of the above

51. Which of the following is a conducting polymer?
    a. Polyaniline
    b. Polyacetylene

c. Polypyrrole
d. All of the above

52. The conducting form of polyaniline is
a. leucoemarldine.
b. emeraldine base.
c. pernigraniline.
d. emeraldine salt.

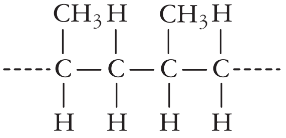
Fill in the Blanks

1. Polymerization of styrene to form polystyrene takes place through _______ polymerization.
2. _______ polymerization requires the presence of two functional groups at both the ends of the monomer.
3. _______ is used in electrical appliances because of its insulation property.
4. A polymer with random arrangement of functional groups around the main chain is called _______ polymer.
5. _______ polymerization is used for the preparation of stereospecific polymers.
6. In _______ polymerization, a polymer of high molecular weight is formed near the end of polymerization.
7. Polymerization between styrene and butadiene would lead to the formation of a _______.
8. The _______ is directly dependent on the molecular weight of the polymer.
9. In _______ polymerization, uncontrolled exothermic reaction may lead to an explosion.
10. Melamine–formaldehyde resin belongs to the class of _______ resins.
11. Addition of _______ gives strength and rigidity to rubber.
12. The essential requirement for a polymer to be intrinsically conducting polymer is the presence of _______.
13. Trans-1,4-polyisoprene is known as _______, while is 1,4-polysioprene is known as _______.
14. Polymerization of butadiene with acrylonitrile yields _______ rubber, whereas that with styrene yields _______ rubber.

Review Questions

Short-Answer Questions

1. What are polymers? How are they classified on the basis of structure?
2. List three advantages and three disadvantages of polymers as compared to traditional materials.
3. How are polymers classified based on their thermal behavior?
4. What are copolymers? How are they classified?
5. Justify the following:
   a. All simple molecules cannot be used as monomers to form polymers.
   b. It is not possible to assign an exact molecular weight to a polymer.
6. Identify the monomers in the following polymers:
   a.

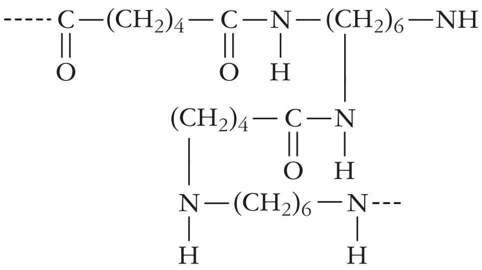


$$\begin{array}{ccccccccc} & CH_3 & & H & & CH_3 & & H & \\ & | & & | & & | & & | & \\ \text{-----} & C & — & C & — & C & — & C & \text{-----} \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

b. 

$$\text{-----}CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}\text{-----}$$

c.



7. How are polymers classified on the basis of mechanism of polymerization? Name and give structures of copolymers formed by reaction of the following monomers:
   - a. Ethylene glycol + Terephthalic acid
   - b. Butadiene + Acrylonitrile
   - c. Hexamethylenediamine + Adipic acid
8. Write the structure and name of homopolymers formed by the following monomers:
   - a. Tetrafluoroethylene
   - b. Isoprene
   - c. ε-Caprolactum
9. What is a syndiotactic polymer? Give an example.
10. Explain the term "functionality" of a monomer with an example.
11. What is a condensation polymer? Give examples.
12. With suitable examples differentiate between isotactic, syndiotactic and atactic polymers.
13. What are graft and block copolymers? Give examples.
14. How can the molecular weight of polymer be controlled in condensation and addition polymerization processes?
15. State the differences between addition and condensation polymerizations?
16. What is meant by degree of polymerization?
17. Explain copolymerization with suitable examples.
18. What are initiators in the free radical polymerization process? Give one specific example.
19. In case of polymerization of a radical, how can you get a low molecular weight polymer?
20. Write the structure of four addition polymers and four condensation polymers with their respective monomers.
21. Explain any one of the mechanisms of addition polymerization using a suitable example.
22. Account for the following:
   - a. Thermal control in solution polymerization is easier compared to bulk polymerization.
   - b. Polymer separates out in form of pearls or beads in suspension polymerization.
23. What is tacticity? How polymers classified are based on tacticity?
24. What is the effect of cross-linking and branching on the properties of polymers?
25. Discuss the structure–property relationship of polymers with respect to (a) tensile strength and (b) crystallinity.
26. What is glass transition temperature? What is its significance?
27. List the factors affecting glass transition temperature (T_g).
28. Write the merits and demerits of using plastics in place of metals.
29. Distinguish between high and low density polyethylenes.
30. Explain why
   - a. Plexiglass is used for manufacture of lenses.
   - b. Teflon-coated utensils are used for cooking.
   - c. PVC is generally plasticized.

31. Name three important thermoplastic resins, along with their structure and polymerization reactions.
32. Name two important thermosetting resins and give their polymerization reactions.
33. What are silicone resins and their important applications?
34. Give the reactions for the formation of polyethylene terephthalate and mention its three important uses.
35. Write a note on urea–formaldehyde resin.
36. Identify the thermosets and thermoplastics among the following: (a) PVC, (b) polyethylene, (c) silicone resins, (d) polyester fiber and (e) bakelite.
37. Write a note on properties and uses of teflon.
38. Write the structures, two properties and two uses of (a) PE, (b) PVC, (c) PTFE and (d) nylon-6,6.
39. Explain why bakelite cannot be remolded.
40. Explain the differences between a thermoset and thermoplastic material with examples.
41. Write down any two distinguishing features of PVC.
42. Write the repeating unit in bakelite, PVC and nylon.
43. What is a plasticizer? What is its main function? Give two examples.
44. Write the structures (only) of the following polymers: (a) polyacrylonitrile, (b) Buna-S, (c) dacron and (d) nylon-6.
45. Why is teflon highly chemical resistant?
46. Write structures of nylon-6,6 and nylon-6. Why are they so named?
47. The DP of PMMA is 1000. What would be the molecular weight of polymethyl methacrylate?
48. Classify the following into different types of polymeric material, giving a method of preparation (equations only): (a) PVC and (b) nylon-6,6 and (c) nylon-6.
49. Give the applications of polyurethanes.
50. Give chemical reactions involved in the preparation of the following types of rubbers along with their structures:
    a. Styrene rubber (GR-S or Buna-S)
    b. Nitrile rubber (GR-A or Buna-N)
    c. Natural rubber
51. Write a short note on rubber and vulcanization. Give structure of vulcanized rubber.
52. How is thiokol prepared? Mention its uses.
53. Mention any two important compounding ingredients of rubber.
54. What are the advantages of synthetic rubber over natural rubber? Name a few synthetic rubbers.
55. How does Buna-S differ from Buna-N?
56. Write a short note on synthetic rubbers. How does butyl rubber differ from Buna-S?
57. What are acrylic fibers? List their important uses.
58. What are carbon fibers? What are the properties and important applications of carbon fiber reinforced composites?
59. What are the characteristics of fiber reinforced plastics (FRP)?
60. What are conducting polymers? How is an organic polymer converted into a conducting polymer?
61. How are conducting polymers classified? Give three important engineering applications of conducting polymers.
62. Write the name and formula of a conducting polymer.

Long-Answer Questions

1. What are polymers? What are the different criteria for their classification?
2. Explain with examples, the classification of polymers based on (a) chemical structure, (b) ultimate physical form and use and **(c)** nature of origin.
3. Describe the steps involved in addition polymerization proceeding by free radical mechanism with the example of formation of polyethylene.
4. Discuss the mechanism for polymerization of isobutene by cationic polymerization.
5. Discuss the mechanism of anionic polymerization considering the example of formation of polymethyl methacylate starting from methyl methacrylate.
6. What is coordination addition polymerization? Discuss the steps involved and significant features of this mechanism.
7. Explain the mechanism for condensation polymerization with a suitable example.
8. Write the differences between
   - **a.** Additional polymerization and condensation polymerization.
   - **b.** Thermosets and thermoplasts.
9. Define polymerization. Explain solution and suspension polymerization techniques.
10. What are the different types of molecular weights for polymers? How are they determined and expressed mathematically?
11. Discuss how the structure of the polymers is related to their properties?
12. What is glass transition temperature? Explain the factors that affect glass transition temperature and mention its significance
13. Explain the manufacturing of LDPE and HDPE, list their properties and mention applications.
14. Explain the manufacture of (a) amino resins and (b) silicone resins and mention their uses.
15. Describe the method of preparation, properties and application of (a) polyvinyl chloride and (b) polytetrafluoro ethylene.
16. What are important thermosetting plastics/ resins? Describe the method of preparation, properties and applications of (a) phenol–formaldehyde resins and (b) urea–formaldehyde resins.
17. What is bakelite? How is it manufactured and mention its uses.
18. Describe the preparation, properties and engineering uses of polyethylene.
19. Why are silicones called inorganic polymers? Discuss the synthesis of linear-chain silicones.
20. What are polyurethanes? Discuss the preparation, properties, uses and applications of polyurethane.
21. Give the synthesis and uses of (a) butyl rubber (b) neoprene (c) Buna-S (d) nitrile rubber (e) polysulphide rubber and (f) silicone rubber.
22. What is vulcanization of rubber? How does it improve the properties of natural rubber?
23. Give methods of preparation and important uses of the following synthetic rubbers:
   - **a.** Styrene rubber (Buna-S or GR–S rubber)
   - **b.** Polyurethane (PU)
   - **c.** Butyl rubber (GR-I)
24. Explain the procedures used in the processing of natural rubber.
25. What are elastomers? Give the preparation, properties and uses of Buna-S.
26. What are fibers and their important properties? Give different types of fibers with examples.

27. Describe the method of preparation, properties and important uses of (a) nylon-6,6, (b) dacron and (c) acrylics.

28. Give preparation, properties, uses and applications of polyesters.

29. Describe the preparation and flowsheet diagram of nylon-6,6.

30. Describe the method of preparation, important properties and applications of epoxy resins.

31. **a.** What are conducting polymers? How they are classified?
    b. Explain the mechanism of conducting in polyacetylene.

32. Mention the different forms of polyaniline and explain the mechanism.

Numerical Problems

1. Calculate the degree of polymerization of styrene, given that number average molecular weight is 2.4×10^4 g/mol.

2. Deduce the molecular formula of the copolymer obtained by copolymerization of 216 g of butadiene with 104 g styrene.

3. What are the number average and weight average molecular weights for a mixture of four molecules with molecular weights 2×10^5 g/mol, 3×10^5 g/mol, 4×10^5 g/mol and 5×10^5 g/mol?

4. Calculate the number average $(\overline{M}_n)$ and weight average $(\overline{M}_w)$ molecular weight of polyvinyl chloride sample with following composition:

$$-\!\!\left[CH_2 - CH \right]\!\!-_{100} \quad -25\%$$
$$-\!\!\left[CH_2 - CH \right]\!\!-_{200} \quad -30\%$$
$$-\!\!\left[CH_2 - CH \right]\!\!-_{400} \quad -45\%$$

5. A polymer sample contains 10% molecules with molecular weight 1000 g/mol, 30% molecules with molecular weight 5000 g/mol; 50% molecules with molecular weight 10,000 g/mol and 10% molecules with molecular weight 20,000 g/mol. Calculate the number average and weight average molecular weights and polydispersity index of the polymer.

6. Calculate the number of molecules of polypropylene formed when 63 g of propene was polymerized by radical polymerization and degree of polymerization was found to be 1.5×10^3.

Answers

Multiple-Choice Questions

1. (c)
2. (c)
3. (b)
4. (d)
5. (b)
6. (c)
7. (a)
8. (c)
9. (d)
10. (d)
11. (a)
12. (b)
13. (c)
14. (d)
15. (c)

16. (d)
17. (b)
18. (d)
19. (a)
20. (d)
21. (c)
22. (a)
23. (c)
24. (a)
25. (b)
26. (c)
27. (b)
28. (c)
29. (a)
30. (b)
31. (b)
32. (c)
33. (b)
34. (d)
35. (b)
36. (a)
37. (d)
38. (d)
39. (a)
40. (b)
41. (c)
42. (a)
43. (a)
44. (b)
45. (c)
46. (d)
47. (a)
48. (a) and (c)
49. (c)
50. (d)
51. (d)
52. (d)

Fill in the Blanks

1. addition
2. Condensation
3. Bakelite
4. atactic
5. Coordination
6. step growth
7. copolymer
8. tensile strength
9. bulk
10. amino
11. reinforcing fillers
12. conjugated π-electron system
13. gutta-percha, natural rubber
14. Buna-N, Buna-S

Numerical Problems

1. 2.3×10^{-2}
2. $C_{24}H_{32}$
3. 3.5×10^5 and 3.85×10^5 g/mol
4. 62.5 g/mol
5. 8600; 11.3×10^3 g/mol; 10^3
6. 10^3 molecules

Appendix A

Atomic Weights of the Elements

Z	*Symbol*	*Name*	*Atomic Wt.*	*Z*	*Symbol*	*Name*	*Atomic Wt.*
1	H	Hydrogen	1.00794(7)	30	Zn	Zinc	65.409(4)
2	He	Helium	4.002602(2)	31	Ga	Gallium	69.723(1)
3	Li	Lithium	[6.941(2)]	32	Ge	Germanium	72.64(1)
4	Be	Beryllium	9.012182(3)	33	As	Arsenic	74.92160(2)
5	B	Boron	10.811(7)	34	Se	Selenium	78.96(3)
6	C	Carbon	12.0107(8)	35	Br	Bromine	79.904(1)
7	N	Nitrogen	14.0067(2)	36	Kr	Krypton	83.798(2)
8	O	Oxygen	15.9994(3)	37	Rb	Rubidium	85.4678(3)
9.	F	Fluorine	18.9984032(5)	38	Sr	Strontium	87.62(1)
10	Ne	Neon	20.1797(6)	39	Y	Yttrium	88.90585(2)
11	Na	Sodium	22.989770(2)	40	Zr	Zirconium	91.224(2)
12	Mg	Magnesium	24.3050(6)	41	Nb	Niobium	92.90638(2)
13	Al	Aluminium	26.981538(2)	42	Mo	Molybdenum	95.94(2)
14	Si	Silicon	28.0855(3)	43	Tc	Technetium	[98]
15	P	Phosphorus	30.973761(2)	44	Ru	Ruthenium	101.07(2)
16	S	Sulphur	32.065(5)	45	Rh	Rhodium	102.90550(2)
17	Cl	Chlorine	35.453(2)	46	Pd	Palladium	106.42(1)
18	Ar	Argon	39.948(1)	47	Ag	Silver	107.8682(2)
19	K	Potassium	39.0983(1)	48	Cd	Cadmium	112.411(8)
20	Ca	Calcium	40.078(4)	49	In	Indium	114.818(3)
21	Sc	Scandium	44.955910(8)	50	Sn	Tin	118.710(7)
22	Ti	Titanium	47.867(1)	51	Sb	Antimony	121.760(1)
23	V	Vanadium	50.9415(1)	52	Te	Tellurium	127.60(3)
24	Cr	Chromium	51.9961(6)	53	I	Iodine	126.90447(3)
25	Mn	Manganese	54.938049(9)	54	Xe	Xenon	131.293(6)
26	Fe	Iron	55.845(2)	55	Cs	Cesium	132.90545(2)
27	Co	Cobalt	58.933200(9)	56	Ba	Barium	137.327(7)
28	Ni	Nickel	58.6934(2)	57	La	Lanthanum	138.9055(2)
29	Cu	Copper	63.546(3)	58	Ce	Cerium	140.116(1)

(*Continued*)

(Continued)

Z	*Symbol*	*Name*	*Atomic Wt.*	*Z*	*Symbol*	*Name*	*Atomic Wt.*
59	Pr	Praseodymium	140.90765(2)	73	Ta	Tantalum	180.9479(1)
60	Nd	Neodymium	144.24(3)	74	W	Tungsten	183.84(1)
61	Pm	Promethium	‘[145}	75	Re	Rhenium	186.207(1)
62	Sm	Samarium	150.36(3)	76	Os	Osmium	190.23(3)
63	Eu	Europium	151.964(1)	77	Ir	Iridium	192.217(3)
64	Gd	Gadolinum	157.25(3)	78	Pt	Platinum	195.078(2)
65	Tb	Terbium	158.92534(2)	79	Au	Gold	196.96655(2)
66	Dy	Dysprosium	162.500(1)	80	Hg	Mercury	200.59(2)
67	Ho	Holmium	164.93032(2)	81	Tl	Thallium	204.3833(2)
68	Er	Erbium	167.259(3)	82	Pb	Lead	207.2(1)
69	Tm	Thulium	168.93421(2)	83	Bi	Bismuth	208.98038(2)
70	Yb	Ytterbium	173.04(3)	90	Th	Thorium	232.0381(1)
71	Lu	Lutetium	174.967(1)	91	Pa	Protactinium	231.03588(2)
72	Hf	Hafnium	178.49(2)	92	U	Uranium	238.02891(3)

Source: IUPAC Commission on Atomic Weight and Isotopic Abundances Values from the 2001 table. *Pure and Applied Chemistry* 75, 1107 (2003). Numbers in parenthesis are uncertainties in least significant digit. For Li, terrestrial sample variations prevent a more precise value. For Te and Pm, no stable isotopes exist.

Appendix B

Fundamental Constants

Constant	*Symbol*	*Value (SI Units)*	*cgs-esu or Other Units*
Gas constant	R	8.31447 J/K/mol 8.31447 m^3 Pa/K/mol	8.31447×10^7 erg/K/mol 0.0820575 L atm/K/mol 1.98721 cal/K/mol
Avogadro's number	N_A	6.02214×10^{23}/mol	6.02214×10^{23}/mol 6.02214×10^{23} amu/g
Faraday constant	F	96485.3 C/mol 96.4853 kJ/V/mol	23.06055 kcal/V/mol
Speed of light	c	2.99792458×10^8 m/s	$2.99792458 \times 10^{10}$ cm/s
Planck's constant	h	6.62607×10^{-34} J s	6.62607×10^{-27} erg s
Boltzmann's constant	k_B	1.38065×10^{-23} J/K	1.38065×10^{-16} erg/K
Electronic charge	e	1.602176×10^{-19} C	4.803204×10^{-10} esu (statC)
Coulomb's law constant	k	8.98755×10^9 J m/C^2	1 erg cm/esu^2
Electron mass	m_e	9.10938×10^{-31} kg	9.10938×10^{-28} g 0.0005485799 amu
Proton mass	m_p	1.672622×10^{-27} kg	1.672622×10^{-24} g 1.0072765 amu
Neutron mass	m_n	1.674927×10^{-27} kg	1.674927×10^{-24} g 1.0086649 amu
Gravitational constant	G	6.673×10^{-11} J m/kg^2	6.673×10^{-8} erg cm/g^2
Acceleration of gravity	g	9.80665 m/s^2	980.665 cm/s^2

Source: P.I. Mohr and B.N. Taylor *Reviews of Modern Physics* 72, 351 (2000).

Appendix C

Conversion Factors

Energy into joules (J)

4.184 J/cal 1.602×10^{-19} J/eV   101.325 J/(L atm) 10^{-7} J/erg 1.986×10^{-23} J/cm^{-1}

Length into meters (m)

10^{-10} m/Å   0.0254 m/in   0.3048 m/ft   1609.3 m/mi

Volume into cubic meters (m^3)

10^{-3} m^3/L 3.7854×10^{-3} m^3/gal

Pressure into pascals (Pa)

101,325 Pa/atm 10^5 Pa/bar   133.3 Pa/torr   6895 Pa(lb/in^2)

Mass into kilograms (kg)

0.4536 kg/lb 1.66054×10^{-27} kg/amu

About the Book

The Chemistry course for undergraduate engineering students is designed to strengthen the fundamentals of chemistry and then build an interface of theoretical concepts with their industrial/engineering applications. This book is structured keeping in view the objective of the course and is intended as a textbook for first year engineering students of Biju Patnaik University of Technology (BPUT) and Siksha 'O' Anusandhan University (S'O'A).

The book aims to impart students an in-depth knowledge of various aspects of chemistry as applied to engineering. It deals with basic principles of chemistry like atomic structure and chemical bonding. The coverage extends to important concepts in physical and inorganic chemistry and includes additional topics on polymers and spectroscopy.

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    - ✓ Comprehensively covers the applied topics in the field of engineering.
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    - ✓ Ample illustrations and diagrams.
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    - ✓ Solved examples at the end of relevant subtopics to strengthen the concepts.
- Comprehensive question bank at the end of each chapter containing:
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    - ✓ Review questions (categorized into short-answer and long-answer type questions).
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