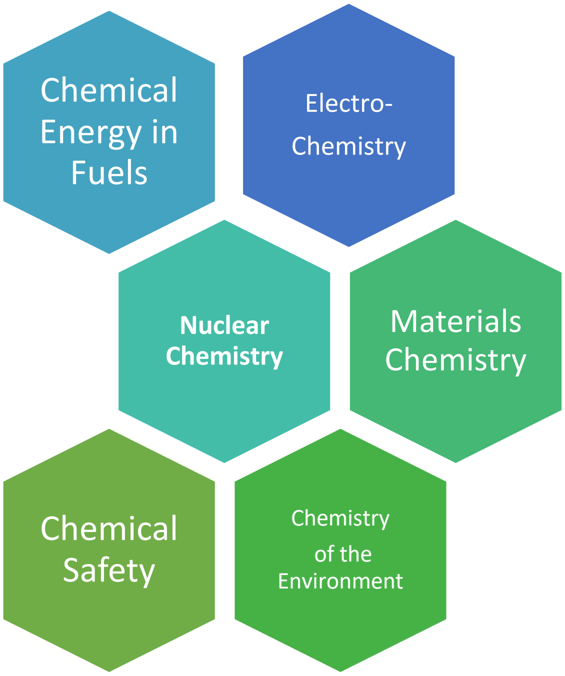


CHEM20024: Chemistry For Engineers

Instructional Material for Correspondence Mode

Department of Physical Sciences, College of Science, Polytechnic University of the Philippines

Jim R. Cruz, RCh
Ferrie S. Oliva, RChE
Henry A. Peralta, RChE
Jose Mari M. Felicita, RCh
Dalton R. Fortin, RCh, MSc
Elizabeth P. Bisa, RChE, MSChE
Florence Joie F. Lacsa, RChE, LPT, MSc

POLYTECHNIC UNIVERSITY OF THE PHILIPPINES
College of Science
DEPARTMENT OF PHYSICAL SCIENCES

COURSE TITLE	: Chemistry for Engineers
COURSE CODE	: CHEM20024
CREDIT UNITS	**:** Three (3) credit units for lecture with a contact time is three (3) hours per week. One (1) credit unit for laboratory with a contact time of three (3) hours per week.
COURSE PREREQUISITE	**:** This course requires prior knowledge and skills on topics as specified in the General Chemistry 1 & 2 and Mathematics 1 and 2 of the Department of Education's Kto12 Basic Education Curriculum – Senior High School Science, Technology, Engineering and Mathematics (STEM) Specialized Strand or bridging-courses equivalent offered by the Polytechnic University of the Philippines.
COURSE DESCRIPTION	**:** The course Chemistry for Engineers is designed to discuss the introductory core concepts of chemistry needed in the field of engineering. It is subdivided into three major parts: (1) energy, which is further comprised of chemical energy from fuel, electrochemistry and nuclear chemistry (2) the chemistry of engineering materials; and (3) the chemistry of the environment. Also included is a discussion on chemical safety.

Institutional Learning Outcomes	Program Outcomes	Course Outcomes
1. **Creative and Critical Thinking** Graduates use their imaginative as well as a rational thinking abilities to life situations in order push boundaries, realize possibilities, and deepen their interdisciplinary and general understanding of the world.	**1. Creative and Critical Thinking**	**1. Creative and Critical Thinking** Students apply the principles of chemistry in energy generation, explain the chemical principles underlying the bonding and structures of common engineering materials, discuss the chemical processes that takes place in the environment and incorporate the elements of chemical safety in their day-to-day lives.
2. **Effective Communication** Graduates are proficient in the four macro skills in communication (reading, writing, listening, and speaking) and are able to use these skills in solving problems. Making decisions, and articulating thoughts when engaging with people in various circumstances.	**2. Effective Communication**	**2. Effective Communication** Students are confident and articulate in delivering ideas and solutions to problems, both in oral and written communication, using chemistry principles involving in energy production and enhancement, materials research and development, environmental preservation and chemical safety.
3. **Strong Service Orientation** Graduates exemplify the potentialities of an efficient, well-rounded and responsible professional deeply committed to service excellence.	**3. Strong Service Orientation**	**3. Strong Service Orientation** Students are efficient and responsible in the application of chemistry principles in the fields of energy, materials, environment and safety.
4. **Community Engagement** Graduates take an active role in the promotion and fulfillment of various advocacies (educational, social and environmental) for the advancement of community welfare.	**4. Community Engagement**	**4. Community Engagement** Students share their learned knowledge on the chemistry principles on their application to energy enhancement, materials development, environmental sustainability and chemical safety to the community.
5. **Adeptness in the Responsible Use of Technology** Graduates demonstrate optimized use of digital learning abilities, including technical and numerical skills.	**5. Adeptness in the Responsible Use of Technology**	**5. Adeptness in the Responsible Use of Technology** Students use current and state-of-the art technologies to better understand concepts and deliver applications of chemistry in the field of energy, materials, environment and safety.
6. **Passion to Lifelong Learning** Graduates are enabled to perform and function in the society by taking responsibility in their quest to know more about the world through lifelong learning.	**6. Passion to Lifelong Learning**	**6. Passion to Lifelong Learning** Students keep their selves abreast on the current trends and practices on energy enhancement, materials research and development, environmental preservation and chemical safety.
7. **High Level of Leadership and Organizational Skills** Graduates are developed to become the best professionals in their respective disciplines by	**7. High Level of Leadership and Organizational Skills**	
	8. Sense of Personal and Professional Ethics	
	9. Sense of National and Global Responsiveness	

manifesting the appropriate skills and leaderships qualities. 8. **Sense of Personal and Professional Ethics** Graduates show desirable attitudes and behavior either in their personal and professional circumstances. 9. **Sense of National and Global Responsiveness** Graduates' deep sense of national compliments the need to live in a global village where one's culture and other people culture are respected.		**7. High Level of Leadership and Organizational Skills** Students enhanced leadership and organizational skills are displayed. **8. Sense of Personal and Professional Ethics** Students display good behavior and desirable attitudes both in their personal and professional lives. **9. Sense of National and Global Responsiveness** Students identify themselves as part of a greater whole; hence, are responsible and accountable of their own actions.

Course Plan: Lecture

Week	Topic	Learning Outcomes	Methodology	Resources	Assessment
1	Orientation and Chemical Safety 1.) Course syllabus 2.) Chemical Safety a) Chemical Safety and its importance b) Hazard versus Risk c) Hazard classification d) Chemical hazard communication: GHS Labelling, NFPA Hazard Identification System and GHS Safety Data Sheet e) Hierarchy of Hazard Controls f) Personal Protective Equipment for Chemical Safety g) Preparing for Emergencies	At the end of the discussion, the students are expected to: 1.) Summarize the course content that would serve as their basis of preparing for different learning activities that are to be conducted during the class 2.) Demonstrate Chemical Safety and discuss its importance. 3.) Differentiate "hazard" and "risk". 4.) Enumerate, discuss and give examples of different hazard classifications. 5.) Explain what does GHS stands for and its importance. 6.) Enumerate and discuss the different elements that compose the GHS label template. 7.) Identify the type of hazard(s) that is (are) being represented by the different GHS pictograms. 8.) Interpret the NFPA Hazard Identification System. 9.) Demonstrate the knowledge on the use of the Safety Data Sheet. 10.) Enumerate and discuss the different hierarchy of hazard controls. 11.) Demonstrate knowledge on the use of Personal Protective Equipment for Chemical Safety 12.) Demonstrate knowledge on preparedness during emergencies.	(1) Lecture (2) Discussion (3) Recitation	https://www.osha.gov/dsg/hazcom/ghsguideoct05.pdf http://www.unece.org/trans/danger/publi/ghs/ghs_rev01/01files_e.html https://www.acs.org/content/acs/en/chemical-safety/basics/nfpa-hazard-identification.html	(1) Quiz (2) Recitation (3) Examination *Applicable only to Chemical Safety
2 - 6	Chemical Energy in Fuels 1.) Fuels and Energy	At the end of the discussion, the students are expected to:	(1) Lecture (2) Discussion	Brown, Lawrence and Holme, Thomas, (2011)	(1) Quiz (2) Recitation

	a) Types of fuels b) Relationship of fuel and energy c) Application of stoichiometry in combustion reactions 2.) Thermodynamic Concepts a) Thermodynamic system b) Thermodynamic states and properties c) Thermodynamic processes d) Units used in the study of Thermodynamics 3.) Thermochemistry a) The Joule's Experiment b) Internal Energy, Heat and Work c) The Mathematical Formulation of the First Law d) The PV-work e) Enthalpy f) Enthalpies of reaction g) Hess' Law of Constant Heat Summation h) Heat capacity i) Calorimetry 4.) Chemical Thermodynamics a) Spontaneity b) Entropy and its physical concept c) The Second and Third Law of Thermodynamics d) Entropy changes in chemical Reactions e) Gibbs Free Energy, temperature and the equilibrium constant 5.) Introduction to heat engines	1.) Define what a fuel is. 2.) Cite the different classifications of fuels. 3.) Discuss how fuels generate energy and explain why do they have different energy values. 4.) Define what is octane number and discuss its relationship with engine knocking. 5.) Differentiate the different calorific values and their means of determination. 6.) Discuss the relationship of the First and Second Laws of Thermodynamics to energy production from fuels. 7.) Distinguish combustion reactions from other types of chemical reactions. 8.) Write combustion reactions properly. 9.) Demonstrate the ability to solve problems involving the application of stoichiometry in combustion reactions. 10.) Define and give examples of the different classifications of a system. 11.) Define and give examples of extensive and intensive properties. 12.) Define what is a state function. 13.) Define and differentiate the different thermodynamic processes. 14.) Define and give examples of the different classifications of a system. 15.) Define and give examples of extensive and intensive properties. 16.) Define what is a state function. 17.) Define and differentiate the different thermodynamic processes. 18.) Covert different thermodynamic parameters across different systems of measurements 19.) Solve problems related to thermodynamic parameters such as, but not limited to, temperature, pressure, density, and work. 20.) Derive different equations for solving pressure 21.) Interpret the First Law of Thermodynamics into its different forms of statements including its correct mathematical formulation. 22.) Describe the concept and importance of the Joule's experiment. 23.) Demonstrate the understanding of internal energy concepts and its relationship to heat and work. 24.) Solve problems on PV-work of a system.	(3) Recitation	*Chemistry for Engineering Students*, 2nd Edition, Brooks/Cole Cengage Learning, USA Brown, T.L., Lemay Jr., H.E., Bursten, B.E., Murphy, C.J., and Woodward, P.M. (2012) *Chemistry: The Central Science*, 12th Ed., USA: Pearson Education, Inc. Chang, Raymond (2010), *Chemistry*, 10th Edition, McGraw-Hill Companies, Inc., USA Smith, J.M., Van Ness, H.C., Abbot, M.M. (1996) *Introduction to Chemical Engineering Thermodynamics*, 5th Ed., McGraw Hill International Editions, Chemical Engineering Series, Singapore Spielberg, M.S. (c2007) *Principles of General Chemistry*, 2nd Edition, New York, USA. Tordillo, J. (2019) *Simplified Engineering Thermodynamics For Thermodynamics 1 and* 2, Tordillo Publising, Cebu City, Philippines	(3) Examination

		25.) Demonstrate the understanding on the concept of enthalpy through problem solving activities. 26.) Interpret thermochemical equations and enthalpy diagrams properly. 27.) Solve problems involving Hess Law of Heat Summation. 28.) Demonstrate an ability to solve involving enthalpies of reaction. 29.) Define heat capacity and discuss its importance. 30.) Solve problems related to heat capacity of a system. 31.) Demonstrate the understanding of the First Law of Thermodynamics as applied in calorimetry. 32.) Solve problems involving calorimetry. 33.) Distinguish between spontaneous and nonspontaneous processes 34.) Describe the dispersal of matter and energy that accompanies certain spontaneous processes 35.) Define entropy. 36.) Explain the relationship between entropy and the number of microstates 37.) Predict the sign of the entropy change for chemical and physical processes 38.) Define Gibbs free energy, and describe its relation to spontaneity 39.) Calculate free energy change for a process using free energies of formation for its reactants and products 40.) Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products 41.) Explain how temperature affects the spontaneity of some processes 42.) Relate standard free energy changes to equilibrium constants 43.) Explain the concept behind the operation of heat engines 44.) Solve problems involving heat engine efficiency.			
7-8	Energy and Nuclear Chemistry 1.) Definitions in Nuclear Chemistry 2.) Types of Nuclear Decay 3.) Kinetics of Nuclear Reaction	At the end of the discussion, the students are expected to: 1.) Describe the five common types of nuclear decay.	(1) Lecture (2) Discussion (3) Recitation	Brown, Lawrence and Holme, Thomas, (2011) *Chemistry for Engineering Students*, 2nd Edition, Brooks/Cole Cengage Learning, USA	(1) Quiz (2) Recitation (3) Examination

	4.) The Mass – Energy Equivalence 5.) Nuclear Transmutation 6.) Nuclear Fission and Fusion 7.) Nuclear Radiation 8.) Applications of Nuclear Reactions	2.) Predict the product of a nuclear decay reaction. 3.) Compute for the half – life or the decay constant of a nuclear reaction. 4.) Apply the use of radioactivity to predict the amount of a sample to the emitted radiation of the sample. 5.) Predict if a nuclide is stable, or what type of decay it will undergo if unstable. 6.) Describe a radioactive series using the nuclide chart. 7.) Evaluate if a positron emission or a beta decay would happen in a given decay. 8.) Define nuclear binding energy and mass defect. 9.) Apply the mass – energy equivalence equation to calculate energies contained in nuclear reactions. 10.) Describe a nuclear transmutation. 11.) Apply the shorthand notation on describing a nuclear transmutation. 12.) Predict missing components of a nuclear transmutation. 13.) Describe a nuclear fission reaction and a nuclear fusion reaction. 14.) Apply the mass – energy equivalence to demonstrate the energy release of these reactions. 15.) Describe the properties of radiation. 16.) Compare the penetration capabilities of ionizing radiation. 17.) Describe types pf nuclear accidents by their scope. 18.) Discuss various applications of nuclear reactions in medicine, food, and other industries.		Brown, T.L., Lemay Jr., H.E., Bursten, B.E., Murphy, C.J., and Woodward, P.M. (2012) *Chemistry: The Central Science*, 12th Ed., USA: Pearson Education, Inc. Chang, Raymond (2010), *Chemistry*, 10th Edition, McGraw-Hill Companies, Inc., USA	
9	Midterm Examinations				
10 -12	Electrochemistry 1.) Fundamentals of electrochemistry 2.) Standard Cell Potential 3.) Thermodynamics in Electrochemistry 4.) Batteries 5.) Corrosion	At the end of the discussion, the students are expected to: 1.) Balance redox reactions in acidic or basic media. 2.) Identify the two general types of cell: voltaic cells and electrolytic cells. 3.) Construct cell notations from chemical equations or cell diagrams.	(1) Lecture (2) Discussion (3) Recitation	Brown, Lawrence and Holme, Thomas, (2011) *Chemistry for Engineering Students*, 2nd Edition, Brooks/Cole Cengage Learning, USA Brown, T.L., Lemay Jr., H.E., Bursten, B.E., Murphy, C.J., and	(1) Quiz (2) Recitation (3) Examination

	6.) Electrolysis	4.) Determine the cell potential of redox reactions 5.) Apply the concept of diagonal rule in determining the spontaneity of redox reacting species. 6.) Determine the correlation of Gibbs Free Energy and the equilibrium constant on the spontaneity of redox reactions. 7.) Derive and apply the equations for non-standard state: the Nernst equation. 8.) Recognize and understand how batteries work and how their applications. 9.) Explain the corrosion process and ways to protect metals from it. 10.) Demonstrate how to make nonspontaneous redox reactions possible through electrolysis. 11.) Demonstrate the quantitative aspects of electrolysis and its application in electroplating.		Woodward, P.M. (2012) *Chemistry: The Central Science*, 12th Ed., USA: Pearson Education, Inc. Chang, Raymond (2010), *Chemistry*, 10th Edition, McGraw-Hill Companies, Inc., USA	
13 - 15	Chemistry of Engineering Materials 1.) Molecular Picture of Materials a) Mechanical Properties of Materials b) Intermolecular Forces c) Phase Diagrams 2.) Simple Atomic Crystal Structure a) Characteristics of Solid Materials b) Crystal Lattices c) Physical Properties of Unit Cell Geometry 3.) Typical Solid State Materials a) Metals b) Semiconductors c) Polymers d) Composites e) Nanomaterials	At the end of the discussion, the students are expected to: 1.) Recognize the different utility of materials by their varying properties 2.) Deconstruct the Intermolecular Forces (IMF) involved in different phases of matter 3.) Utilize Phase Diagrams of pure substances and mixtures 4.) Differentiate apparent bulk characteristics of amorphous and crystalline structures. 5.) Describe the types of crystal lattices and apply geometry in their dimensional character. 6.) Compute material density using unit cell geometry and formula weights. 7.) Demonstrate understanding of basic crystal diffraction utilizing Bragg's Law. 8.) Demonstrate understanding of the electronic properties in metals and semiconductors through the Band Theory. 9.) Visualize the macromolecule of polymers and compute their molecular weights. 10.) Explain the effects of internal structure in composites and nanomaterials.	(1) Lecture (2) Discussion (3) Recitation	Callister Jr., W., (2007) *Material Science and Engineering: An Introduction*, John Wiley & Sons, USA Masteron, W.L., and Hurley, C.N. (2008) *Chemistry: Principles and Reactions*, 6th edition. Canada: Brooks/Cole-Cengage Learning Whitten, K.W., Davis, R.E., Peck, M.L. and Stanley G.G (2010) Chemistry 9th Edition. USA, Brooks/Cole-Cengage Learning	(1) Quiz (2) Recitation (3) Examination
16-17	The Chemistry of the Environment 1.) The chemistry of the atmosphere a) The composition of the earth's atmosphere.	At the end of the discussion, the students are expected to: 1) Describe how the different layers of the atmosphere are characterized.	(1) Lecture (2) Discussion (3) Recitation	Brown, Lawrence and Holme, Thomas, (2011) *Chemistry for Engineering Students*, 2nd Edition,	(1) Quiz (2) Recitation (3) Examination

	b) The processes in atmosphere c) Air pollutants, their sources and effects. 2.) The chemistry of the hydrosphere a) The composition of the earth's hydrosphere b) The processes in the hydrosphere c) Water pollutants, their sources and effects 3.) The chemistry of the lithosphere a) The composition of the Lithosphere b) The processes in the lithosphere c) Soil pollutants, their sources and effects	2) Discuss how the change in the lapse rate at the troposphere affect the life on earth. 3) Enumerate the components of the atmosphere. 4) Describe the impact of the processes in the troposphere on air quality. 5) Discuss how the stratospheric ozone works. 6) Describe how aerosols affect the earth's temperature and climate. 7) Enumerate the ten groups of air pollutants and discuss their respective sources and effects. 8) Discuss how the incomplete internal engine combustion adds to air pollution. 9) Describe how greenhouse gases enhance the greenhouse effect. 10) Discuss the chemical reactions behind photochemical smog formation, stratospheric ozone destruction and acid rain formation. 11) Describe the importance of water. 12) Explain the properties of water with respect to its composition and structure. 13) Discuss the different processes within the hydrological cycle. 14) Label the different water bodies with their approximate global distribution. 15) Differentiate the classifications of natural waters according to their sources. 16) Describe how the different natural waters are formed. 17) Discuss how the different factors affect the water quality. 18) Describe the different sources of water pollutants. 19) Discuss the impacts of each of the pollutants to the bodies of water and the organisms living in them. 20) Differentiate the structures and composition of the solid earth. 21) Discuss the composition and the importance of the lithosphere. 22) Differentiate the three different classifications of rocks and their sub-classifications. 23) Discuss the processes on how the different rock classifications are formed. 24) Describe how the rock cycle works.		Brooks/Cole Cengage Learning, USA Brown, T.L., Lemay Jr., H.E., Bursten, B.E., Murphy, C.J., and Woodward, P.M. (2012) *Chemistry: The Central Science*, 12th Ed., USA: Pearson Education, Inc. Chang, Raymond (2010), *Chemistry*, 10th Edition, McGraw-Hill Companies, Inc., USA Ibanez, J.G., Hernandez-Esparza, M., Doria-Soriano, C., Fregoso-Infante, A., Singh,M.M. (2007) *Environmental Chemistry Fundamentals*, Springer Science+Business Media, LLC, New York, USA Synder, Carl H., (2003), *The Extraordinary Chemistry of Ordinary Things*, 4th Edition, John Wiley & Sons, Inc, USA	

		25) Define the process of weathering and its importance. 26) Differentiate the three classifications weathering. 27) Describe how the different mechanical weathering processes take place. 28) Describe how the different chemical weathering processes take place. 29) Illustrate how pollutants lead to soil contamination. 30) Provide suggestions for better landfill usage.			
18	Final Examination				

Course Plan: Laboratory

Week	Topic	Learning Outcomes	Methodology	Resources	Assessments
1	Orientation 1. Laboratory safety guidelines and regulations 2.. Common laboratory equipment and apparatus	At the end of the orientation period, the students are expected to: (a) Summarize the course content that would serve as their basis of preparing for different learning activities that are to be conducted during the class (b) Recall and demonstrate the guidelines and regulations for laboratory safety (c) Recall the common laboratory equipment and apparatus and their specific uses.	(1) Lecture (2) Discussion	Beran, J.A. **(2009)** *Laboratory Manual for Principles of General Chemistry*, 8th edition John Wiley and Sons Inc. Burg, D.L. (2013) *Laboratory Manual For General Chemistry*. Dephlogisticated Columbus, Ohio *CHED Memorandom Order No. 18, Series of 2007*, for the BS Chemistry Program Hill, R.H.Jr. and Finster, D.C. (2010) *Laboratory Safety for Chemistry Students*. John Wiley and Sons Inc Polytechnic University of the Philippines – College of Science Safety Guidelines and Regulations	(1) Quiz (2) Recitation (3) Examination
2-3	Experiment 01: Measurement	At the end of the orientation period, the students are expected to:	(1) Discussion (2) Laboratory Experiment	Chang, R. and Goldsby, K. **(2019).** *Chemistry*. 13th international ed. New York: McGraw Hill Education	(1) Recitation (2) Examination (3) Laboratory reports

		(a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use. (b) Demonstrate to properly use and handling laboratory instruments and apparatus. (c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment. (e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived from the experiment. (g) Solve problems involving applications on the concept of measurement including the conversion of one measurement unit to the other, across different systems.		Masteron, W.L., and Hurley, C.N. (2008) *Chemistry: Principles and Reactions*, 6th edition. Canada: Brooks/Cole-Cengage Learning Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual Weiner, S.A and Harrison, B. **(2010)** *Introduction to Chemical Principles: A Laboratory Approach* Brooks Cole Cengage Learning	
4-5	Experiment 02: Heat of Combustion	At the end of the orientation period, the students are expected to: (a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use. (b) Demonstrate to properly use and handling laboratory instruments and apparatus. (c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment. (e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived from the experiment (g) Examine and formulate a conclusion on the relationship of fuel property to the amount of energy it contains.	(1) Discussion (2) Laboratory Experiment	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Laboratory reports
6-7	Experiment 03: Calorimetry	At the end of the orientation period, the students are expected to: (a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use. (b) Demonstrate to properly use and handling laboratory instruments and apparatus.	(1) Discussion (2) Laboratory Experiment	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Laboratory reports

		(c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment. (e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived from the experiment. (g) Examine and formulate a conclusion how does the First Law of Thermodynamics is applied in calorimetry.			
8	Activity 01: Nuclear reactions, Binding Energy and Rate of Decay	At the end of the orientation period, the students are expected to: (a) Independently solve problems on nuclear reactions, binding energy and rate of decay. (b) Present solutions to problem solving materials given in a clear and orderly manner.	(1) Discussion (2) Problem solving activity	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Problem sets
9	Midterm Examination				
10	Experiment 04: Electrolytic Cells and Batteries	At the end of the orientation period, the students are expected to: (a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use. (b) Demonstrate to properly use and handling laboratory instruments and apparatus. (c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment. (e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived from the experiment. (g) Examine and formulate a conclusion on the relationship of redox reactions to the energy productions in cells and batteries.	(1) Discussion (2) Laboratory Experiment	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Laboratory reports
11	Experiment 05: Corrosion	At the end of the orientation period, the students are expected to: (a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use.	(1) Discussion (2) Laboratory Experiment	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Laboratory reports

		(b) Demonstrate to properly use and handling laboratory instruments and apparatus. (c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment. (e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived from the experiment. (g) Examine and formulate a conclusion on the relationship of redox reactions to metal corrosion.			
12-13	Experiment 06: Polymers: An Investigation on Its Mechanical Properties	At the end of the orientation period, the students are expected to: (a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use. (b) Demonstrate to properly use and handling laboratory instruments and apparatus. (c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment. (e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived from the experiment. (g) Examine and formulate a conclusion on the various factors that affects the mechanical properties of polymers.	(1) Discussion (2) Laboratory Experiment	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Laboratory reports
14	Activity 02: Crystal Lattices and Unit Cells	At the end of the orientation period, the students are expected to: (a) Independently solve problems on nuclear reactions, binding energy and rate of decay. (b) Present solutions to problem solving materials given in a clear and orderly manner.	(2) Problem solving activity	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Problem sets
15	Experiment 09: Air Quality Monitoring	At the end of the orientation period, the students are expected to:	(1) Discussion (2) Laboratory Experiment	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Laboratory reports

		(a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use. (b) Demonstrate to properly use and handling laboratory instruments and apparatus. (c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment. (e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived from the experiment (g) Construct a simple means of monitoring air quality.			
16	Experiment 08: Water Properties and Its Purification	At the end of the orientation period, the students are expected to: (a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use. (b) Demonstrate to properly use and handling laboratory instruments and apparatus. (c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment. (e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived from the experiment. (g) Construct a simple but efficient water filtration apparatus.	(1) Discussion (2) Laboratory Experiment	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Laboratory reports
17	Experiment 09: Determination of Dissolved Oxygen Content in Water	At the end of the orientation period, the students are expected to: (a) Demonstrate the ability to choose appropriate laboratory instruments and apparatus based on their intended use. (b) Demonstrate to properly use and handling laboratory instruments and apparatus. (c) Demonstrate proper handling and disposal of chemicals used in the experiment. (d) Demonstrate the knowledge on chemical safety during the conduct of the experiment.	(1) Discussion (2) Laboratory Experiment	Polytechnic University of the Philippines - Chemistry for Engineers Laboratory Manual	(1) Recitation (2) Examination (3) Laboratory reports

		(e) Construct a laboratory report based on the data and observations that were carefully and honestly derived from the experiment. (f) Demonstrate appreciation of the application that was derived. (g) Demonstrate how dissolved oxygen in water is determined.			
18	Final Examinations				

Suggested Readings and References

Beran, J.A. **(2009)** *Laboratory Manual for Principles of General Chemistry*, 8th edition John Wiley and Sons Inc.

Brown, Lawrence and Holme, Thomas, (2011) *Chemistry for Engineering Students*, 2nd Edition, Brooks/Cole Cengage Learning, USA

Brown, T.L., Lemay Jr., H.E., Bursten, B.E., Murphy, C.J., and Woodward, P.M. (2012) *Chemistry: The Central Science*, 12th Ed., USA: Pearson Education, Inc.

Burg, D.L. (2013) *Laboratory Manual For General Chemistry*. Dephlogisticated Columbus, Ohio

Callister Jr., W., (2007) *Material Science and Engineering: An Introduction*, John Wiley & Sons, USA

Chang, Raymond (2010), *Chemistry*, 10th Edition, McGraw-Hill Companies, Inc., USA

Chang, R. and Goldsby, K. **(2019).** *Chemistry*. 13th international ed. New York: McGraw Hill Education

CHED Memorandum Order No. 18, Series of 2007, for the BS Chemistry Program

CHED Memorandum Order No. 87, Series of 2017, for the BS Computer Engineering Program

CHED Memorandum Order No. 88, Series of 2017, for the BS Electrical Engineering Program

CHED Memorandum Order No. 92, Series of 2017, for the BS Civil Engineering Program

CHED Memorandum Order No. 96, Series of 2017, for the BS Industrial Engineering Program

CHED Memorandum Order No. 76, Series of 2017, for the BS Mechanical Engineering Program

CHED Memorandum Order No. 76, Series of 2017, for the BS Electronics and Engineering Program

Ibanez, J.G., Hernandez-Esparza, M., Doria-Soriano, C., Fregoso-Infante, A., Singh,M.M. (2007) *Environmental Chemistry Fundamentals*, Springer Science+Business Media, LLC, New York, USA

Masteron, W.L., and Hurley, C.N. (2008) *Chemistry: Principles and Reactions*, 6th edition. Canada: Brooks/Cole-Cengage Learning

Polytechnic University of the Philippines – College of Science Safety Guidelines and Regulations

Roussack, O.V., Gesser. H.D., (2013). *Applied Chemistry: A Textbook of Engineers and Technologists*, 2nd Ed., London, Springer

Smith, J.M., Van Ness, H.C., Abbot, M.M. (1996) *Introduction to Chemical Engineering Thermodynamics*, 5th Ed., McGraw Hill International Editions, Chemical Engineering Series, Singapore

Spielberg, M.S. (c2007) *Principles of General Chemistry*, 2nd Edition, New York, USA.

Synder, Carl H., (2003), *The Extraordinary Chemistry of Ordinary Things*, 4th Edition, John Wiley & Sons, Inc, USA

Tordillo, J. (2019) *Simplified Engineering Thermodynamics For Thermodynamics 1 and* 2, Tordillo Publising, Cebu City, Philippines

Weiner, S.A and Harrison, B. **(2010)** *Introduction to Chemical Principles: A Laboratory Approach* Brooks Cole Cengage Learning

Whitten, K.W., Davis, R.E., Peck, M.L. and Stanley G.G (2010) Chemistry 9th Edition. USA, Brooks/Cole-Cengage Learning

https://www.osha.gov/dsg/hazcom/ghsguideoct05.pdf

http://www.unece.org/trans/danger/publi/ghs/ghs_rev01/01files_e.html

https://www.acs.org/content/acs/en/chemical-safety/basics/nfpa-hazard-identification.html

Course Grading System

The students who are enrolled in Chemistry for Engineers should get a grade of 3.0 or better to get the four (4) credit units.

Final Grade = (Midterm Grade + Tentative Final Grade) / 2							
Midterm Grade				Tentative Final Grade			
Lecture Grade		Laboratory Grade		Lecture Grade		Laboratory Grade	
75%		25%		75%		25%	
Class Standing	Examination	Class Standing	Examination	Class Standing	Examination	Class Standing	Examination
70%	30%	70%	30%	70%	30%	70%	30%

Classroom Policy

The faculty-in-charged has the prerogative to implement his/her class policies provided that such are agreeable with and/or not showing superiority against the rules and regulations being implemented by the Polytechnic University of the Philippines.

Consultation Time

Please refer to the posted schedule of the faculty’s consultation hours.

Prepared by:

Engr. Ferrie S. Oliva
Mr. Jim R. Cruz, RCh
Engr. Henry A. Peralta
Mr. Jose Mari M. Felicita, RCh
Engr. Florence Joie F. Lacsa, LPT, MSc
Faculty Members, Department of Physical Sciences

Reviewed by:

Engr. Elizabeth P. Bisa, MSChE
Chairperson, Department of Physical Sciences

Recommending Approval:

Dr. Lincoln A. Bautista
Dean, College of Science

Approved by by:

Dr. Emmanuel C. de Guzman
Vice President for Academic Affairs

Revised August 2020

INTRODUCTION TO THE SUBJECT

The course **Chemistry for Engineers** is designed to discuss the introductory core concepts of chemistry needed in the field of engineering. It is subdivided into three major parts: (1) energy, (2) the chemistry of engineering materials; and (3) the chemistry of the environment. It also includes a discussion on Chemical Safety.

The discussion on **Chemistry and Energy Relationship** is further divided into (a) fuels, (b) nuclear chemistry and (c) electrochemistry. In here the relationship of chemistry to the formation of energy is discussed. Under the subject *Chemical Energy in Fuels*, students will get to familiarize themselves with various kinds of fuel that are being used in the industrial and engineering applications. After which, they are to explore the underlying principles that exists between chemical reactions and energy – the fields of thermochemistry and solutions thermodynamics. In addition, discussion on *Nuclear Chemistry* includes lessons on how radioactivity can be used in the production of energy. Furthermore, the relationship that exists between chemical reactions and electricity is explored under *Electrochemistry*.

The relationship existing between materials' property, performance and structure is explained under the section of the **Chemistry of Engineering Materials** wherein emphasis is given to *metals, semiconductors, polymers, composites* and *nanomaterial*. Prior to the discussion on the aforementioned materials, the basic concepts of *crystal structures* are first explored.

The key chemical processes that takes place in the environment is the main topic under the **Chemistry of the Environment** wherein the chemistry of the *atmosphere, hydrosphere* and *lithosphere* are discussed.

Moreover, the subject has its **laboratory** component which gives the students the chance to experience experiments that will enhance the knowledge gained from the lecture classes. With this, basic knowledge and principles on handling of chemicals are also discussed under *Chemical Safety.* This also serves as their introductory course for safety in the workplace and other places wherein Chemical Safety is needed.

Guidelines on the Use of this Instructional Material

A. General Guidelines

1. This instructional material is designed for students who are enrolled under Chem20024: Chemistry for Engineers and opted to undergo the correspondence mode (offline) of learning.

2. No part of this material should be copied nor distributed without the consent of the authors.

3. This material is strictly not for sale as it is intended for instructional purposes only.

4. “Chemistry for Engineers” is a specialized course that requires sufficient knowledge and skills on General Chemistry, Algebra, Trigonometry, Plane Geometry and Basic Differential and Integral Calculus. It is the student’s responsibility to do the review on the basic concepts that are needed to better understand the subject matter discussed herein.

5. This course is a combination of chemistry and mathematics. No student can solve problems that are included in this course without the aid of a Periodic Table of Elements and a scientific calculator. It is expected that the student will provide his/her own aforementioned materials.

6. Reference materials and any other kind of material indicated herein is not the professor’s responsibility to provide for the student.

7. The student is expected to make a schedule on how he or she will undergo with the course. The course syllabus can be used as a guide to which part of this instructional material should be studied based on the semester workweek.

8. This course has a laboratory component; hence, it is a requirement for the student to conduct the laboratory experiments that are included herein.

9. Included experiments can be done at home. While household materials are to be used in the conduct of the experiments, it is the student’s responsibility to provide those that are not readily available in their own homes.

10. Chemical Safety is the first discussion that the student needs to go through. It is expected that the safety protocols learned from there are to be observe during the conduct of the experiments.

B. Grading System

1. For the student to get the full four (4) credit units, he should get a grade of 3.0 or better.

2. For a passing mark, the student should get at least 50% of the correct answers from the given activities.

3. The formula for the calculation of grade can be found in the course syllabus.

4. Points for Class Standing will coming from the Activities and Assessments found in the end of every lesson.

5. Points for the Examination component will be coming from the summative examination found after the Lecture and Laboratory portions of this module.

C. Guidelines on the Accomplishment and Submission of Activities

1. The student is REQUIRED to submit answers to ALL of the “Activities and Assessment” section found in this module on or before the prescribed deadline. Non-submission on or before the deadline means no credit.

2. All answers should be HAND-WRITTEN and in INK (blue or black ONLY) in a LONG BOND PAPER following the prescribed format. Please refer to the next page for the format of the *ANSWER SHEET FOR ACTIVITIES AND ASSESSMENT*.

3. Each question should be answered in SEPARATE pages of the answer sheets.

4. For problem solving item, FINAL ANSWERS should be expressed using the CORRECT NUMBERS OF SIGNIFICANT FIGURES and should be ENCLOSED inside a box. The solutions should be COMPLETELY shown and should be presented in an organized manner.

CHEMISTRY FOR ENGINEERS
ANSWER SHEET FOR ACTIVITIES AND ASSESSMENT

LESSON/ACTIVITY/EXPERIMENT. & TITLE:	
UNIT NO. & TITLE:	
NAME:	DATE OF ACCOMPLISHMENT:
ID NO.:	PAGE NO:
YEAR/COURSE/SECTION:	TOTAL NUMBER OF PAGES:

CONTENTS

CHEMISTRY OF THE ENVIRONMENT

PART B: LABORATORY

PART D: APPENDICES

LECTURE

LESSON 01: CHEMICAL SAFETY
Unit 01: Hazard and Its Classifications

Introduction:

“Safety First”. This is a slogan that can usually be seen in workplaces which signifies the need to prioritize safety above anything else in the work environment. The safety of the working individuals is very important because it is directly related to the productivity of not just the workers but of the institution. In addition, a safe workplace also entails reduction on costs related to the decrease in working capacity and/or to the increase in accidental insurance. Above all, human life is essential; it must be taken care of.

As future engineers, the workplace is where most of the day is spent and it is where exposure to different types of hazards may be experienced and many will be work as leaders who are to oversee the safety of his or her subordinates. With this, a basic knowledge on how safety protocols work is needed, as part of protecting ourselves and others.

Chemical safety refers to the condition of being safe from undergoing hurt or harm during an occurrence of chemical incident. A chemical incident is an unintentional event that may threaten to expose or do expose members of the public to a chemical hazard.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Demonstrate “Chemical Safety” and discuss its importance.
2. Differentiate the terms “hazard” and risk”.
3. Enumerate, discuss and give examples of different hazard classifications.

Course Materials:

<u>What is a hazard?</u>

Hazard is defined as any source of potential harm, damage or adverse effect on someone of something. For instance, (1) a fast-running vehicle is a hazard to a person who is crossing the same road the vehicle is moving on; (2) a poorly treated industrial wastewater is a hazard to the body of water where the wastewater is being dumped; (3) an x-ray radiation is a hazard to a radio technologist operating the machine.

Risk, on the other hand, is the probability that a person or a thing is harmed or damaged when exposed to a hazard. It talks about (1) the chance of the person crossing a road be hit by a fast moving vehicle, (2) the chance of the body of water to be polluted from the harmful substance present in the wastewater and (3) the chance that the radio technologist get a disease caused by his exposure to the x-ray radiation. The higher the risk, the higher the probability of getting harmed from the exposure to the hazard.

How are hazards classified?

1. ***Physical hazards*** are factors within the environment that may cause harm on the body even without touching it and they are generally discernible and perceptible. Examples are slippery floors, poor lighting, and excessive noise.

2. ***Chemical hazards*** refer to the chemical substances that may cause harm upon exposure to them. Examples are gases, fumes and liquids.

3. ***Ergonomic hazards*** are physical factors in the environment that may cause problems on the musculoskeletal system. Examples are poor workstation design, repetitive movements and poor workflow.

4. ***Radiation hazards*** are the factors in the environment that causes exposure to the emission of electromagnetic waves. Examples are x-rays, ultraviolet rays and lasers.

5. ***Psychological hazards*** are the aspects of the working environment that may affect the mental health of the individuals such as workload, stress and discrimination.

6. ***Biological hazards*** are biological substances that may threat the health of living organisms exposed to it such as viruses, bacteria and animals.

What are Hazardous Substances?

According to Occupational Safety and Health Administration (OSHA) of the United States of America, a ***hazardous substance*** is any chemical that presents physical or health hazard.

Under OSHA's Health Communication Standard (HCS), ***physical hazard*** means a chemical that is a combustible liquid, a compressed gas, explosive, flammable, an organic peroxide, an oxidizer, pyrophoric, unstable (reactive) or water-reactive. Physical hazards are classified as fire hazard, reactive hazard and explosion hazard.

On the other hand, ***health hazard*** means a chemical that may cause acute or chronic health effects to exposed personnel. They are classified as either systematic effect or target organ effect.

According to Republic Act 6969, a substance is hazardous when it present either a short-term acute hazard or long-term chronic toxicity. ***Acute hazards*** are those that have obvious and immediate impact while ***chronic hazards*** are those that have more hidden, cumulative and long-term impact.

Activities and Assessments:

1. In your own words, define what chemical safety is and state its importance to your life as (1) a member of the community, (2) a student of Chemistry for Engineers who is to undergo laboratory classes; and (3) a future professional working in the engineering field.
2. Cite the difference between "hazard" and "risk" by giving an example.
3. Imagine yourself to be a medical practitioner in a hospital that caters Covid-19 pandemic patients. Name a hazard under each classification that you are exposed to.
4. How would you determine if a substance is hazardous or not?
5. What is the difference between a physical from chemical hazard? Between chronic and acute hazard?

LESSON 01: CHEMICAL SAFETY
Unit 02: Hazard Communication: GHS Labeling

Introduction:

Hazardous substances are those that cause harmful or adverse effects to those that they are exposed to. However, these can be minimized, if not prevented, through their proper and appropriate handling which can be done by proper communication using standard chemical labels.

In this part of the lesson, you will be introduced to the GHS labelling which is the standard means of communication on hazardous substances that is being used around the world as established by the United Nations.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Explain what does "GHS" stands for and its importance.
2. Enumerate and discuss the different elements that compose the GHS label template.
3. Identify the type of hazard(s) that is (are) being represented by the different GHS pictograms.

Course Materials:

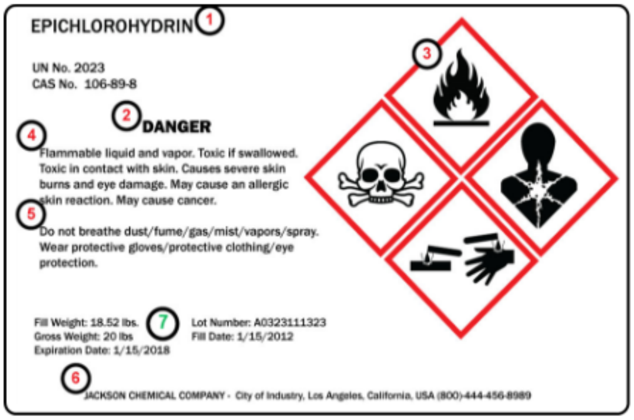
The GHS Labels

Adapted from "Globally Harmonized System of Classification and Labelling of Chemicals" by the United Nations.

One of the administrative controls being employed is the proper handling of chemicals through proper chemical labeling. It must be recalled that a "chemical" is a substance that is used or is produced in a reaction involving changes of atoms and molecules. Adding labels to the chemicals will the user the idea on how to properly handle or use it.

GHS stands for Globally Harmonized System of Classification and Labeling of Chemicals. It is an internationally agreed-upon system created by the United Nations that requires manufacturers, importers and downstream users and distributors of chemical substances and mixtures.
GHS was started to be adopted in June 1, 2015. The establishment of GHS had an objective of unifying the communication on hazardous products and of replacing the specific regulations in countries around the world.

The ***GHS label template*** has the following standardized elements according to "Globally Harmonized System of Classification and Labeling of Chemicals (GHS)" by the United Nations.



EPICHLOROHYDRIN

UN No. 2023
CAS No. 106-89-8

DANGER

Flammable liquid and vapor. Toxic if swallowed. Toxic in contact with skin. Causes severe skin burns and eye damage. May cause an allergic skin reaction. May cause cancer.

Do not breathe dust/fume/gas/mist/vapors/spray. Wear protective gloves/protective clothing/eye protection.

Fill Weight: 18.52 lbs.
Gross Weight: 20 lbs
Expiration Date: 1/15/2018

Lot Number: A0323111323
Fill Date: 1/15/2012

JACKSON CHEMICAL COMPANY - City of Industry, Los Angeles, California, USA (800)-444-456-8989

Figure 1: GHS Label Template [Image source: www.nicelabel.com]

1. ***Product Name or Identifier***: This is the name of the substance contained inside the labeled container.

2. ***Signal word***: This is a single word which can either be "Warning" or "Danger". It is used to indicate the relative severity of the product wherein "Danger" indicates more severe hazards and "Warning" for less severe hazards.

3. ***Precautionary symbols or pictogram(s):*** Show(s) a representation of the classification of chemical hazard the product has to expose to its user.

4. ***Physical, Health and Environmental Hazard statements***: Standardized and assigned phrases that describes the hazard based on its classification.

5. ***Precautionary measures:*** Provides the measures to be undertaken to minimize the effect from product exposure. This include the first aid measures that are needed to be undertaken and the appropriate personal protective equipment to be used when dealing with it.

6. ***Supplier identification:*** Gives the name, address and contact details of the manufacturer.

7. ***Supplemental Information***: Includes additional information that the customer requests to include.

The GHS Pictograms and Their Representations

Physical hazards	Fire hazards	Oxidizing solids Oxidizing liquids Oxidizing gases	
		Flammable solids Flammable liquids Flammable gases Flammable aerosols Substances which in contact with water, emits flammable gases Pyrophoric solids Pyrophoric liquids	
	Reactive hazards	Self-heating substances	
		Self-reactive substances Organic peroxides	 
		Corrosive to metals	
	Explosion hazards	Explosives	
		Gases under pressure	

Health hazards	Systemic effects	Skin corrosion	
		Skin irritation Eye irritation Serious eye damage Dermal sensitization	
		Acute toxicity	
	Target organ effects	Carcinogenicity Respiratory sensitization Reproductive toxicology Target organ systemic toxicity Germ Cell Mutagenicity Aspiration toxicity	
Environmental Hazards	Acute aquatic toxicity Chronic aquatic toxicity		

Oxidizers can either be solids, liquids or gases. They are materials that are not necessarily combustible but may generally yield oxygen which may contribute to or cause combustion reactions.

Flammable solids can either be readily combustible or may cause or contribute to fire through friction. They can be in the form of granules, powder and pastry which is easily ignited when come into contact with an ignition source.

Flammable liquids are liquids with flash points of not more than 93°C.

Flammable gases are gases with flammable range in air at 20°C and at standard pressure of 101.3kPa.

Flammable aerosols are any gas that (1) was compressed, liquefied or dissolved under pressure within a non-refillable container that was made up of metal, glass or plastic and (2) contains any component classifies as flammable solid, liquid or gas.

Emits flammable gas are substances that can either solids or liquids that are liable to become spontaneously flammable or to give off flammable gases when get in contact with water.

Pyrophorics are substances which can either be solids or liquids that are liable to ignite within five minutes after having been in contact with air even at very small quantities.

Self-heating substances are solid or liquid substances that are not classified as pyrophorics but is liable to self-heat when comes in contact with air even in the absence of energy.

Self-reactive substances are either (1) thermally unstable liquids or (2) solids that may undergo strong exothermal decomposition even in the absence of the participation of oxygen but (3) are not classified as corrosives, explosive or organic peroxides under the GHS.

Organic peroxides are either solid or liquid substance that contains bivalent O-O structure. These substances may be liable to explosive decomposition, burn rapidly, be sensitive to impact or friction or react dangerously to other substances.

Corrosive to metals are substances that materially damaged metals through chemical reaction

Explosives are substances or mixtures of substances that can either be solids or liquids which in their selves are capable to produce a gas, by a chemical reaction, at such speed as to cause damage to the surroundings.

Gases under pressure are gases that are contained inside a receptacle with a pressure of not less than 280 Pascal at 20°C.

Substances labelled with ***skin corrosion*** are substances that cause irreversible skin damage following an application of a test substance for four (4) hours.

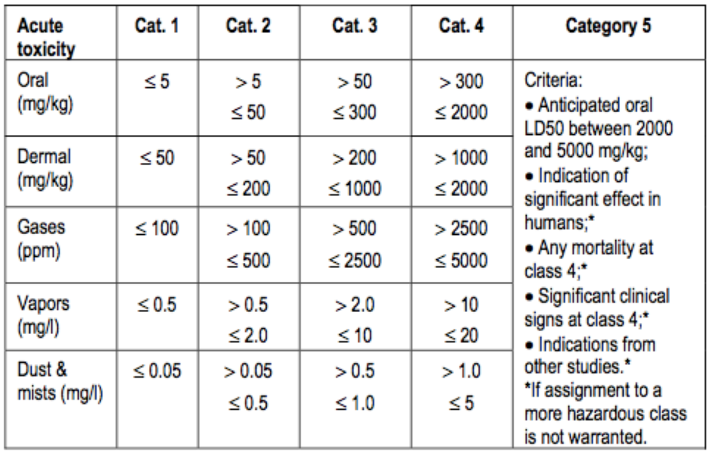
Skin irritation is the label being considered when the substance causes a reversible damage to the skin following an application of a test substance for four (4) hours.

A substance causes ***eye irritation*** if it causes changes in the eye after an application of a test substance to the front surface of the eye, but are fully reversible twenty-one (21) days after the application.

Serious eye damage pertains to the production of eye tissue damage or serious physical decay of vision that is not reversible twenty-one (21) days following the application of the substance.

Dermal sensitization is caused by substances that induce allergic reaction following contact to the skin.

Acute toxicity are substances assigned to the Five Toxicity Categories on the basis of LD50 (oral and dermal) and LC50 (inhalation.)



Acute toxicity	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Category 5
Oral (mg/kg)	≤ 5	> 5 ≤ 50	> 50 ≤ 300	> 300 ≤ 2000	Criteria: • Anticipated oral LD50 between 2000 and 5000 mg/kg; • Indication of significant effect in humans;* • Any mortality at class 4;* • Significant clinical signs at class 4;* • Indications from other studies.* *If assignment to a more hazardous class is not warranted.
Dermal (mg/kg)	≤ 50	> 50 ≤ 200	> 200 ≤ 1000	> 1000 ≤ 2000	
Gases (ppm)	≤ 100	> 100 ≤ 500	> 500 ≤ 2500	> 2500 ≤ 5000	
Vapors (mg/l)	≤ 0.5	> 0.5 ≤ 2.0	> 2.0 ≤ 10	> 10 ≤ 20	
Dust & mists (mg/l)	≤ 0.05	> 0.05 ≤ 0.5	> 0.5 ≤ 1.0	> 1.0 ≤ 5	

Source: A Guide to the Globally Harmonized System of Classification and Labelling of Chemicals", by United Nations

Carcinogens refer to the chemical substances that induce cancer or increase its incidence.

Respiratory sensitizers are chemical substances that cause the airways to be hypersensitive after inhalation of the substance.

Reproductive toxicity may cause infertility, adverse effects on sexual functions and/or developmental toxicity on the offspring.

Target organ systemic toxicity may cause either reversible or irreversible damages on specific body organs which affects their functions.

Germ Cell Mutagenicity may cause gene mutations of organisms to occur.

Aspiration toxicity includes severe acute effects of varying degrees of pulmonary injury or death following aspiration.

Acute aquatic toxicity causes injury to aquatic organisms after a short-term exposure to the substance.

Chronic aquatic toxicity causes adverse effects to aquatic organisms during exposures based on the organism's life cycle.

Activities and Assessments:

1. What does "GHS" means and why is it important?
2. Look for an available GHS-compliant label of hydrogen sulfide, identify the type of hazards of the substances and the necessary measure(s) if someone inhales it.
3. Look for an available GHS-compliant label of n-propyl alcohol, identify the type of hazards of the substances and the necessary measure(s) if it gets to your eyes.

LESSON 01: CHEMICAL SAFETY
Unit 03: Hazard Communication: NFPA Diamond and SDS

Introduction:

The communication on hazardous substances does not stop with the GHS label template. The NPFA diamond is also included which a quick visual representation of the substance's hazards. A standard document that bears a more detailed information on the product's identity, hazards, exposure prevention measures and appropriate response in various situations is also available. It is known as the GHS Safety Data Sheet (SDS). It is used as a primary reference material of individuals who are dealing closely with the chemical as it provides procedures on how to use, store, handle and transport the substance safely.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Interpret the NPFA Hazard Identification System.
2. Demonstrate the knowledge on the use of the Safety Data Sheet.

Course Materials:

<u>NFPA Hazard Identification System</u>

The National Fire Protection Agency Hazard Identification System is a quick visual representation of a chemical substance in terms of its reactivity, flammability, health hazard and special hazards.

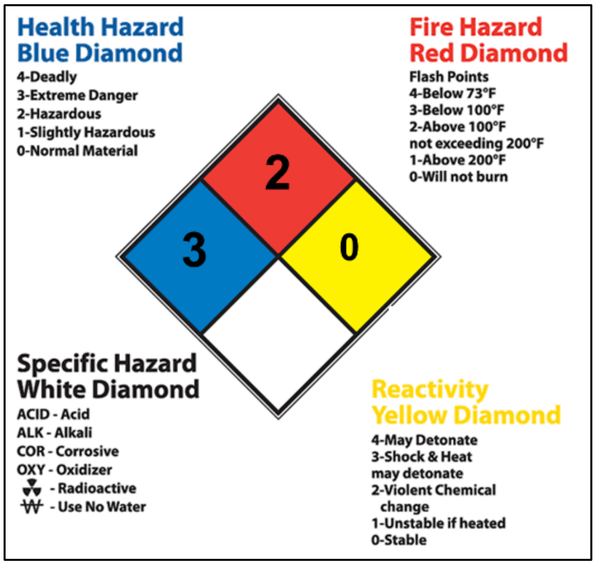


Figure 2: NFPA Hazard Identification System

GHS Safety Data Sheet

Adapted from "Globally Harmonized System of Classification and Labelling of Chemicals" by the United Nations.

The GHS Safety Data Sheet (SDS) provides comprehensive information on the chemical substance being handled. It comprises of the following minimum elements:

1. ***Identification of the substance or mixture and of the supplier***
   Includes the GHS product identifier and other means of product identification, recommended and restricted uses of the product and the supplier's information details.

2. ***Hazards identification***
   Includes the GHS classification of the substance or mixture, GHS label elements and precautionary statements and other hazards that are not covered by GHS.

3. ***Composition or information of ingredients***
   For substances, this include the substance's chemical identity, CAS number, EC number, impurities and stabilizing additives. For mixtures, the chemical identity and concentration of the ingredient(s) which is (are) identified us hazardous, the cut-off levels of reproductive toxicity and, carcinogenicity, mutagenicity and other hazard classes.

4. ***First aid measures***
   Provides description of necessary measures to each of the different routes of exposure (inhalation, skin contact, eye contact and ingestion), the most important symptoms and indications when medical attention or treatment is needed.

5. ***Firefighting measures***
   Provides a list of suitable distinguishing media, the specific hazards arising from the chemicals and the proper protective equipment and precautions needed during firefighting activities.

6. ***Accidental release measures***
   Provides the personal and environmental precautions including the proper personal protective equipment and the appropriate method and materials used during clean ups.

7. ***Handling and storage***
   Provides precautions during handling and the conditions for safe storage.

8. ***Exposure controls and personal protection***
   Shows the control parameters, engineering controls and appropriate personal protective equipment.

9. ***Physical and chemical properties***
   Includes the list of both the physical and chemical properties of the substance such as but not limited to appearance, pH, odor, melting point, initial boiling point, flash point, evaporation rate, flammability, vapor pressure, vapor density, relative density, solubility, auto-ignition temperature and decomposition temperature.

10. ***Stability and reactivity***
    Show the product's stability, possible hazardous reactions, conditions to avoid, incompatible materials and hazardous decomposition products.

11. ***Toxicological information***
    Gives concise but complete information on various toxicological effects, its route of exposure, symptoms and delayed and immediate effects and numerical toxicity scale

12. ***Ecological information***
    Show information of the product's ecotoxicity, persistence and degradability, bio accumulative potential, mobility in soil

13. ***Disposal considerations***
    Gives the description of waste residue and information of its proper handling and disposal.

14. ***Transport information***
    Provides the UN number, UN proper shipping name, transport precautions, identification as marine pollutant, packaging.

15. ***Regulatory information***
    Shows the environmental, safety and health regulations specific to the product.

16. ***Other information***

Before the implementation of the GHS SDS format, manufacturers use the Material Safety Data Sheet (MSDS). Both of the materials have the same element but they differ in content. The GHS SDS format is the one that was discussed in the lesson because it is the one that is more utilized in the industries now a days.

Activities and Assessments:

1. Make an NPFA hazard identification label for a deadly, stable radioactive substance but does not burn.
2. You are to work with a 0.5N hydrochloric acid purchased from LabChem, Inc. The SDS is available for download from the company's website.
    a) Is the product applicable for food use?
    b) Is the product flammable?
    c) What are the personal protective equipment that you need to use when handling the substance?
    d) What is (are) the available GHS pictogram(s) for the product?
    e) What is the first aid measure during skin contact?

LESSON 01: CHEMICAL SAFETY
Unit 04: Hazard Control

Introduction:

While we cannot always run from the presence of hazards, we can always minimize it effect by conducting activities that helps in the control of our exposure. This part of the lesson will give ideas on different measures that are being incorporated to keep ourselves safe from possible effects of our exposure to substances that may have harmful or adverse effects on us and the environment.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Enumerate and discuss the different hierarchy of hazard controls.
2. Demonstrate the knowledge on the use of personal protective equipment.
3. Demonstrate knowledge on preparedness during emergencies.

Course Materials:

<u>The Hierarchy of Hazard Controls</u>

The effect(s) of exposure to chemical hazards can be minimized using different measure of exposure control.

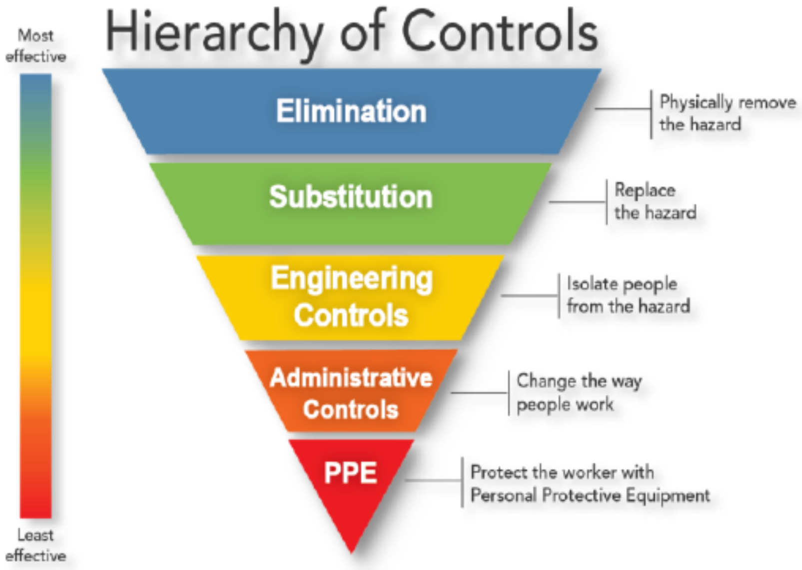


Figure 3: Hierarchy of Hazard Controls. *Image Source: "Chemical Safety Training Course Material" downloaded from https://www.uab.edu/ehs/images/docs/chem/CS101-course-material.pdf*

1. ***Elimination***: This is the most effective means of minimizing the exposure of personnel to a chemical hazard. In here, the hazard is physically removed from the work environment.

2. ***Substitution***: If elimination is not possible, a chemical that is less hazardous is used to replace the existing more hazardous one.

3. ***Engineering Controls***: If the above measures are not available, isolating the people away from the hazard can be done such as the establishment of a safety compartment that separates or limits the exposure of the personnel from the hazard.

4. ***Administrative Controls***: The way people handle the chemicals can also be a means to minimize the effects of being exposed to the harmful substance. Changing the way people work is what comprise the administrative controls.

5. ***Personal Protective Equipment***: Protecting oneself from a hazard with appropriate personal protective equipment is the first line of defense when limiting the exposure from a hazard. However, this method of exposure control is the least efficient of them all.

<u>The Personal Protective Equipment for Chemical Safety</u>

Personal protective equipment (PPE) are garments and devices that serves as a barrier between the user and the hazard being exposed to. There are several types of PPEs available which are classified in terms of their usage. The ones that are included here are those that are specific for chemical safety.

Safety glasses are used whenever there is a chance of objects striking the eye. They are not appropriate protection from a chemical splash.

IMAGE SOURCE: www.sentrysafetysupply.com

Splash goggles are used when working with liquids.

IMAGE SOURCE: www.ebay.com

Face shield with splash goggles when the splash hazard is high, or the chemicals are particularly dangerous.

IMAGE SOURCE www.rockler.com

Figure 4: Personal Protective Equipment for Eye and Face Protections

Personal Protective Equipment (PPE) can be classified according to the part of the body that it intends to protect.

1. Eye and face protection
    a) Safety spectacles
    b) Eye goggles
    c) Face shields
2. Respiratory protection
    a) Filtration respirators
    b) Chemical cartridge devices
    c) Air-supplying equipment
3. Hand and arm protection
    a) Gloves
4. Foot and leg protection
5. Torso protection
    a) Laboratory gowns and coats

However, it should be noted that the use of personal protective equipment has its limitations. Among them are:

1. The use of PPE does not change the fact that the hazard still exists.
2. Wearing a defective PPE offers no protection.
3. Improper wearing of PPE may not give maximum protection.
4. The PPE may be a cause of additional hazard.

Preparing for Emergencies

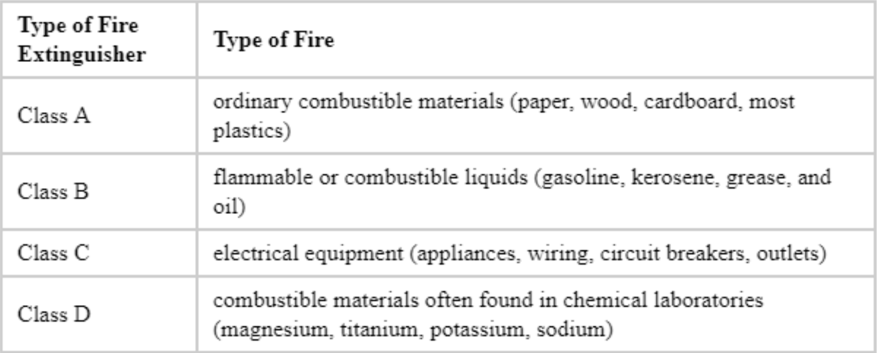
1. In case of burns and small cuts, look for a laboratory first aid kit and treat self accordingly. Go to the nearest clinic or hospital, as the need arises.
2. In case of laboratory spillage, know the property of the substance that you are to deal with. Make sure to use the appropriate spill kit available. Protect yourself with appropriate personal protective equipment. Confine the spill clean it up and properly dispose.

Figure 5: Spill Kit. Image source www.google.com, www.serpro.co.uk

3. In case of chemical splashes, head to the nearest eye wash or eye shower and follow proper procedures as indicated on the product’s SDS.

Figure 6: Eye Wash and Shower Stations. Image sources www.zoro.com, www.texasgateway.org

4. Check on the labels of the available fire extinguishers near the workplace. In case of fire, make sure that you are using the appropriate type.



Type of Fire Extinguisher	Type of Fire
Class A	ordinary combustible materials (paper, wood, cardboard, most plastics)
Class B	flammable or combustible liquids (gasoline, kerosene, grease, and oil)
Class C	electrical equipment (appliances, wiring, circuit breakers, outlets)
Class D	combustible materials often found in chemical laboratories (magnesium, titanium, potassium, sodium)

Figure 7: Fire Extinguisher Classifications *Image source:* www.medisave.co.uk; safetysuppliescanada.com

5. Always put SAFETY FIRST.

Activities and Assessments:

1. What are the different hierarchy of hazard controls? Give an example for each
2. Give situations when you can appropriately use safety glasses, safety goggles and face shields.
3. The lesson on Chemical Safety ends with the slogan “Think Safety First.” Why is this so? How are you going to practice during times of emergencies? Cite an example of a situation to answer the question.

LESSON 02: FUELS AND ENERGY
Unit 01: The Fuel and Energy Relationship

Introduction:

Have you ever wondered how an internal combustion engine makes a vehicle move upon introducing fuel to it? Have you thought of the reason why we become weak when do not eat much food for a day's work? Answers to such queries can be found by going through a discussion on the relationship of fuel and energy.

Lesson Objectives:

After successful completion of this lesson, the students are expected to:

1.) Define what a fuel is.
2.) Cite the different classifications of fuels.
3.) Discuss how fuels generate energy and explain why do they have different energy values.
4.) Define what is octane number and discuss its relationship with engine knocking.
5.) Differentiate the different calorific values and their means of determination.
6.) Discuss the relationship of the First and Second Laws of Thermodynamics to energy production from fuels.

Course Materials:

What is a fuel?

Fuels are dense repositories of energy that are consumed to provide energy services such as heating, transportation and electrical generation.[1] They are substances which when undergoes the process of combustion, will produce energy in the form of heat. Fuels contain elements that are readily combustible (readily reacts with air oxygen) such as carbon and hydrogen.

Classifications of Fuel

Fuels can be classified according to its phases: solid, liquid and gaseous.

A. Solid fuels

   a) Coal

   Coal originated from the arrested decay of the remains of different forms of plant life which flourished in huge swamps and bog millions of years ago.[2]

   b) Coke
   Coke is the solid, cellular, infusible material remaining after the carbonization of coal, pitch and petroleum residues and certain other carbonaceous materials.[2]

   c) Coal Char
   Coal char is the non-agglomerated, non-fusible residue from the thermal treatment of coal.

d) Peat
Peat is partially decomposed plant matter that has accumulated underwater of in a water-saturated environment.[2]

e) Wood
Wood **is** a hard fibrous substance consisting basically of xylem that makes up the greater part of the stems, branches, and roots of trees or shrubs beneath the bark and is found to a limited extent in herbaceous plants.[3]

f) Charcoal
Charcoal is the residue from the destructive distillation of wood.[2]

g) Solid wastes and biomass
Biomass is a plant material and animal waste used especially as a fuel.[3]

B. Liquid fuels

1. Liquid petroleum fuels
Liquid petroleum fuels are made by fractional distillation of crude petroleum which is a mixture of hydrocarbons and hydrocarbon derivatives.[2]

2. Nonpetroleum liquid fuels

   a. Tar sands
   Canadian tar sands are strip-mined and extracted with hot water to recover heavy oil which is further processed into naphtha, kerosene and gasoline fractions.[2]

   b. Oil shale
   Oil shale is nonporous rock containing organic kerosene.

   c. Coal-derived fuels
   Liquid fuels derived from coal range from highly aromatic coal tars to liquids resembling petroleum.

C. Gaseous fuels

1. Natural gas
Natural gas is a combustible gas that occurs in porous rock of the earth's crust and is found with or near accumulations of crude oil.

2. Hydrogen gas
Hydrogen gas is made industrially by the steam reforming of natural gas, as the by-product or industrial operations such as thermal cracking of hydrocarbon and the production of chlorine, and to a lesser extent, by the electrolysis of water.[2]

3. Acetylene
Acetylene is a colorless hydrocarbon with a chemical formula of C_2H_2.[3]

4. Miscellaneous fuels
   This includes reformed gas, oil gases, producer gas, blue water gas, carbureted water gas, coal gas and blast-furnace gas.[2]

An Overview: How do fuels generate energy?

Chemical energy is the interaction energy present between the atomic elements that comprise a material. When the bonds between atoms changes, the energy between them can either be absorbed or released. When the process of absorbing energy is involved, it means that energy is stored. Wood has a stored energy absorbed from the sun which can be released through appropriate processes. With this, we can claim that wood provides energy and can be considered as a fuel.

The energy that is released from the combustion of a fuel is equivalent to the difference of the energy available between the bonds that were broken and the energy that is used in the formation of new bonds that were formed due to the process.

$$Net\ energy = \sum energy\ from\ bond\ breakage - \sum energy\ from\ bond\ formation$$

Consider the combustion of methane (CH_4), a highly combustible hydrocarbon.

$$CH_{4(l)} +\ 2O_{2(g)}\ \rightarrow CO_{2(g)}\ + 2H_2O_{(l)}$$

In the given reaction, the bonds between C-H and O-O are broken down and bonds between C-O and H-O are formed. With this, the energy that is released during the procedure is equivalent to the total energy that exist between the C-H and O-O bonds minus the total energy that exist between the C-O and H-O.

The C-H bond energy is around 410 kJ/mole and the O-O bond energy is 494 kJ/mole. Given this data, the total bond energy that was released due to the breakdown of four (4) C-H bonds and two (2) O-O bond is 2628 kJ/mole. C-O bond energy is around 799 kJ/mole and the H-O bond energy is around 460 kJ/mole. Given this data, the total bond energy that was absorbed due to the formation of two (2) C-O bond and four (4) H-O bond is 3438 kJ/mole. Therefore, net energy released from the combustion of one mole of methane (CH_4) is 810 kJ.

$$Net\ energy = \left[\left(4mol\ x\ \frac{410\ kJ}{mol}\right) + \left(2mol\ x\frac{494\ kJ}{mol}\right)\right] - \left[\left(2\ mol\ x\frac{799\ kJ}{mol}\right) + \left(4\ molx\frac{460\ kJ}{mol}\right)\right]$$
$$= 810\ kJ$$

How does an internal combustion engine work?

The turning on of the ignition of the vehicle produces electric current from the battery which will turn the engine on. When the engine is on, it begins to consume fuel and air. The combustion reaction between the fuel and the air will occur upon firing of the spark plug. The chemical energy that is produced from the combustion reaction is what keeps the engine running.

The ratio of the maximum volume of the gasoline-air mixture ate the beginning of the compression stroke of the engine to the volume of the fully compressed mixture as the spark plug fires at the end of the compression stroke is known as the ***compression ratio***. The higher the compression ratio, the higher the combustion ratio, the more energy is squeeze out of the fuel and the more power the engine can provide.

However, the compression ratio is limited by knocking, that is, the higher the compression ratio, the higher the occurrence of knocking to occur. ***Knocking*** is a rapid pinging or knocking sound that comes from an engine when it is pushed to produce a lot of power quickly. It is a result (1) from an ignition of the mixture before the piston has risen to the point where the spark plug normally fires, (2) from a combustion that begins spontaneously at one or more spots in the cylinder, either before or just as the plug fires, or (3) a combination of the two. Knocking can result to a loss of power, inefficient and uneconomical fuel use and can produce fractures in the top surface of the piston.[4]

Studies show that the more highly branched an alkane is, the greater is its tendency to burn smoothly and evenly and to resist knocking[4]. With this, branched alkanes are blended to the fuel to improve its resistance to knocking. The fuel mixture content is reflected on the fuel's ***octane rating*** or ***octane number***, which is also a measure of the fuel's ability to resist engine knock. The higher the octane number of the fuel, the higher is its ability to resist knocking. Straight chain unbranched alkanes are assigned with low octane numbers because they have a great tendency to knock, while highly branched and aromatic hydrocarbons receive high octane numbers because of their high resistance against knocking.

Octane (C_8H_{18}), a straight-chain hydrocarbon, was used as a reference because it has a highly branched isomer called the 2-2-4-trimethylpentane which has a considerable ability to burn smoothly and resist knocking; therefore, has an assigned octane number of 100. Meanwhile, heptane was assigned with zero octane number because of its great tendency to knock. The combination of 2-2-4-trimethylpentane and heptane is used to evaluate octane ratings.

How does a human engine work?

Metabolism is a complex series of chemical reactions taking place inside a living organism which includes the breaking down of food as its means of producing energy. Carbohydrates, proteins and fats are made up of hydrocarbons which reacts with oxygen to break its bonds to produce energy.

Fuel Calorific Value

Because different fuels have different chemical structures and compositions, they also provide different amount of energy.

The amount of heat that is liberated by a fuel's complete combustion is known as the fuel's calorific value or heating value. The higher the calorific value of a fuel, the higher is the amount of energy that is released from it during the combustion process. Table 1.0 shows different mechanical fuels with their corresponding calorific values while Table2.0 shows the calorific value for food.

Table 1.0 Calorific values of different mechanical fuels.

FUELS	ENERGY CONTENT (Lower Heating Value, BTU/gal)	ENERGY CONTENT (Higher Heating Value, BTU/gal)
Gasoline	112,114 - 116,090	120,388 - 124,340
Low Sulfur Diesel	128,488	138,490
Biodiesel	119,550	127,960
Propane (LPG)	84,250	91,420
Compressed Natural Gas (CNG)	*20,160	*22,453
Liquefied Natural Gas (LNG)	*21,240	*23,726
Ethanol	76,330	84,530
Methanol	57,250	65,200
Hydrogen	*51,585	*61,013

Source: *www.afdc.energy.gov*[5]*;* Note: *BTU/lb

Table 2.0: Calorific Values of Food Content

FUEL	ENERGY CONTENT, calories per gram
Carbohydrates	4
Proteins	4
Fat	9

Source: *www.nal.usda.gov*[6]

The fuel calorific value can be determined using the method of calorimetry through the application of the First Law of Thermodynamics.

Sample Problem 01:

A pouch of a chocolate has 10 grams of fat, 24 grams of carbohydrates and 4 grams of protein. (a) Calculate the total energy, in calories, that this pouch of chocolate can provide.

Solution:

$$Total\ energy = \left(10\ g\ x\ \frac{9\ cal}{g}\right) + \left(24\ g\ x \frac{4\ cal}{g}\right) + \left(4\ g\ x\ \frac{4\ cal}{g}\right) = 202\ cal$$

Fuel Energy and its Relationship to Thermodynamics

The potential energy that can be derived from fuels are transformed into different forms that can be used as a source of power. With this, the energy from the fuel is said to be conserved; hence, follows the First Law of Thermodynamics which is also known as the Law of Conservation of Energy. This thermal energy is taken randomly and is transformed into ordered work by going against the Second Law of Thermodynamics which states that "the entropy of the universe is increasing."

Activities and Assessments:

1.) In your own words, define what is a fuel and how do they generate energy.
2.) Cite the different classifications of fuels. Explain the reason why they have different energy values.
3.) Define what is octane number and discuss its relationship with engine knocking.
4.) Discuss the relationship of the First and Second Laws of Thermodynamics to energy production from fuels.
5.) Look for any food label and calculate the total energy that it can provide.

LESSON 02: FUELS AND ENERGY
Unit 02: The Application of Stoichiometry in Combustion Reactions

Introduction:

When people travel through their vehicles, they fill their engines in with an appropriate amount of fuel to keep their cars running until they reach their desired destinations. The relationship between the amount of fuel needed to release a specific amount of energy is explored under thermochemistry. However, before going to the said topic it is important to have a review on the application of stoichiometry in combustion reactions first. Combustion reactions are means of releasing energy from fuels and stoichiometry is the tool that shows the quantitative relationships among fuels and their products.

Lesson Objectives:

After successful completion of this lesson, the students are expected to:

1) Distinguish combustion reactions from other types of chemical reactions.
2) Write combustion reactions properly.
3) Demonstrate the ability to solve problems involving the application of stoichiometry in combustion reactions.

Course Materials:

A **combustion reaction** involves the reaction of a material with oxygen to produce oxides of all other elements as products releasing energy in the form of heat during the process. It is commonly known as "burning" and it generally goes with the *general equation*:

$$fuel + O_2 \rightarrow CO_2 + H_2O$$

Fuels are usually made up of elements that readily reacts with oxygens such as carbon and hydrogen. Examples of which are butane propane (C_3H_8) and butane (C_4H_{10}), the main components of Liquified Petroleum Gas (LPG).

The combustion reactions are:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$$

Notice that the coefficients of the balanced combustion reactions differ from one reaction to another as a consequence of the Law of the Conservation of Mass which states that matter can neither be created nor destroyed.

Reactants (C_3H_8, O_2)	Elements	Products (CO_2, H_2O)	Reactants (C_4H_{10}, O_2)	Elements	Products (CO_2, H_2O)
1 x 3 = 3	C	3 x 1 = 3	2 x 4 = 8	C	8 x 1 = 8
5 x 2 = 10	O	(3 x 2) + (4 x 1) = 10	13 x 2 = 26	O	(8 x 2) + (10 x 1) = 26
1 x 8 = 8	H	4 x 2 = 8	2 x 10 = 20	H	10 x 2 = 20

The tabulated number of elements show that the number of atoms participating in the reaction is the same as the number of atoms that are present in the product as a result of the process.

From the coefficients of the balanced chemical reaction, one can determine the specific amount of product that is produced from a specific amount of fuel consumed through stoichiometry. Stoichiometry therefore gives us the quantitative relationships among reactants and products in a given chemical reaction.

Take propane for instance. From the balanced chemical reaction, one can say that there are 3 moles of carbon dioxide and 4 moles of water that are produced when one mole of propane burns completely.

Since the number of moles is related to the mass of the substance, the balanced chemical reactions can also give us an idea on the mass of carbon dioxide and mass of water that is produced in every mole of propane.

$$mass = (number\ of\ moles)\ x\ (molecular\ weight)$$

$$mass\ C_3H_8 = 1\ mol\ C_3H_8\ x\ \frac{44\ grams\ C_3H_8}{1\ mol\ C_3H_8} = 44\ grams$$

$$mass\ CO_2 = 3\ mol\ CO_2\ x\ \frac{44\ grams\ CO_2}{1\ mol\ CO_2} = \ 132\ grams$$

$$mass\ H_2O = 4\ mol\ H_2O\ x\ \frac{18\ grams\ O_2}{1\ mol\ H_2O} = 72\ grams$$

With these, we can say that 132 grams of carbon dioxide and 52 grams of water are produced from the complete combustion of 44 grams of propane.

<u>Sample Problem 01:</u>

What mass of carbon dioxide is produced when 105 grams of methane, CH_4 burns completely in air?

Given: 105 grams of methane undergoing complete combustion
Required: mass of carbon dioxide produced

Solution:

$$CH_4 + 2O_2\ \rightarrow\ CO_2 + 2H_2O$$

$$\begin{aligned} &mass\ CO_2 \\ &= given\ mass\ CH_4\ x\ molar\ mass\ of\ CH_4\ x\ stoichiometric\ ratio\ of\ CH_4{:}\,CO_2\ x\ molar\ mass\ CO_2 \end{aligned}$$

$$mass\ CO_2 = given\ mass\ CH_4\ x\ \frac{1\ mole\ CH_4}{mass\ of\ CH_4}\ x\ \frac{1\ mole\ CO_2}{1\ mole\ CH_4} x\ \frac{mass\ CO_2}{1\ mole\ CO_2}$$

$$mass\ CO_2 = 105\ grams\ x\ \frac{1\ mole\ CH_4}{16\ grams\ CH_4}\ x\ \frac{1\ mole\ CO_2}{1\ mole\ CH_4}\ x\ \frac{44\ grams\ CO_2}{1\ mole\ CO_2} = 289\ grams$$

Answer: The mass of CO_2 produced is 289 grams.

<u>Sample Problem 02:</u>

How many grams of ethanol (C_2H_5OH) is needed to produce 150 grams of water when it is subjected to complete combustion?

Given: 150 grams of water produced

Required: mass of ethanol needed

Solution:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$$\begin{aligned} &mass\ C_2H_5OH \\ &= given\ mass\ H_2O\ x\ molar\ mass\ H_2O\ x\ stoichiometric\ ratio\ C_2H_5OH{:}H_2O\ x\ molar\ mass\ C_2H_5OH \end{aligned}$$

$$\begin{aligned} \text{mass}\ C_2H_5OH &= given\ mass\ H_2O\ x\ \frac{1\ mole\ H_2O}{18\ grams\ H_2O} x\ \frac{3\ mole\ C_2H_5OH}{1\ mole\ H_2O} x\ \frac{18\ grams\ C_2H_5OH}{1\ mole\ C_2H_5OH} \\ &= 128\ g \end{aligned}$$

Answer: The mass of ethanol needed is 1289 grams.

<u>Sample Problem 03:</u>

How many moles of carbon dioxide is produced if 10 grams of butane (CH_4H_{10}) burns with 10 grams of oxygen?

Given: 10 grams of butane and 10 grams of oxygen undergoing combustion

Required: mass of carbon dioxide produced

Solution:

$$2C_4H_{10} +\ 13O_2\ \rightarrow\ 8CO_2 + 10H_2O$$

Assume butane as the limiting reactant:

$$\text{mole}\ CO_2 = 10\ grams\ C_4H_{10}\ x \frac{1\ mole\ C_4H_{10}}{58\ grams\ C_4H_{10}} x\ \frac{8\ mole\ CO_2}{2\ mole\ C_4H_{10}} = 0.69\ mole$$

Assume oxygen as the limiting reactant:

$$mole\ CO_2 = 10\ grams\ O_2\ x\ \frac{1\ mole\ O_2}{32\ grams\ O_2}\ x\ \frac{8\ mole\ CO_2}{13\ mole\ O_2} = 0.20\ mole$$

Answer: Since the limiting reactant is oxygen, the amount of carbon dioxide produced is 0.20 mole.

__Sample Problem 04:__

Calculate for the mass (in grams) of carbon dioxide that is produced when a butane gas contained in a 20-liter container at 5 atm and 25°C, burned completely with excess oxygen.

Given: butane gas, V = 20 L, P = 1 atm, T = 25°C undergoing complete combustion

Required: mass of carbon dioxide produced

Solution:

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$$

On the assumption that the butane is an ideal gas,

$$number\ of\ moles, n = \frac{Pressure, P\ x\ Volume, V}{Universal\ Gas\ Constant, R\ x\ Tempertaure, T}$$

$$number\ of\ moles\ of\ butane = \frac{(5\ atm)(20\ L)}{\left(\frac{0.08205\ L-atm}{mol-K}\right)(25°C + 273.15)K}$$

$$number\ of\ moles\ of\ butane = 4\ moles$$

To solve for the amount of carbon dioxide, apply the concept of stoichiometry,

$$mass\ CO_2 = 4\ moles\ C_4H_{10}\ x\ \frac{8\ moles\ CO_2}{2\ moles\ C_4H_{10}}\ x\ \frac{44\ g\ CO_2}{1\ mole\ CO_2} = 704\ grams$$

Answer: The amount of carbon dioxide produced is 705 grams.

Activities and Assessments:

1.) Distinguish which among the following chemical reactions is (are) combustion reaction(s):

   a) $2H_2 + O_2 \rightarrow 2H_2O$
   b) $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
   c) $2C_{12}H_{26} + 37O_2 \rightarrow 24\ CO_2 + 26\ H_2O$
   d) $C_3H_6O + 4O_2 \rightarrow 3CO_2 + 3H_2O$

2.) During combustion, if nitrogen is present in the original fuel, it is converted to N_2, not to a nitrogen-oxygen compound. Write the balanced combustion equation of the fuel dinitroethylene, whose formula is $C_2H_2N_2O_4$.

3.) 100 grams of water was produced from the complete combustion of naphthalene ($C_{10}H_8$). Calculate for the initial volume of the fuel in liters. Assume that it is stored in a container under a pressure of 1 atm and a temperature of 25°C.

LESSON 04: THERMODYNAMIC CONCEPTS
Unit 01: Thermodynamic Measurements and Quantities

Introduction:

Thermodynamic systems are described by measurable quantities such as pressure, volume, temperature and amount of material. This is because a change in any of them may result in a change on the property and state of the system it describes. With this, in the study of thermodynamics, no one can never go away from measurements and its related works.

Lesson objectives:

After successful completion of this lesson, the students are expected to:

1) Covert different thermodynamic parameters across different systems of measurements
2) Solve problems related to thermodynamic parameters such as, but not limited to, temperature, pressure, density, and work.
3) Derive different equations for solving pressure.

Course Materials:

Thermodynamic Quantities

Since the study of thermodynamics involves changes in thermodynamic parameters, it is important to review the different fundamental dimensions and quantities that are involved in such changes.

Dimensions and Units

Measurement is the extent, size, capacity or amount of something as has been determined.[3] It is composed of a magnitude and a unit. The magnitude determines the quantity of something being measured, while the unit determines the physical quantity of being measured.

In 1960, the international community had agreed to use a standard means of measurement in scientific engagements known as SI unites or the Sytème International d'Unitès. The SI base units important in the study of thermodynamics is shown in Table 1.0.

Table 1.0. SI Base Units Important in the Study of Thermodynamics.

Physical Quantities	Definition	Name of Unit	Abbreviation
Mass	the mass of a platinudiridium cylinder kept at the International Bureau of Weights and Measures at Skvres, France.	Kilogram	kg
Length	the distance light travels in a vacuum during 11,299,792,458 of a second.	Meter	m
Time	the duration of 9 192 631 770 cycles of radiation associated with a specified transition of the cesium atom.	Second	S

Temperature	equal to 11273.16 of the thermodynamic temperature of the triple point of water	Kelvin	K
Amount of substance	the amount of substance represented by as many elementary entities (e.g., molecules) as there are atoms in 0.012 kg of carbon-12.	Mole	mol

These base units can be combined with each other to form the **derived units**. Common SI derived units in the field of thermodynamics are shown in Table 2.0.

Table 2.0. Common SI Derived Units Used in Thermodynamics

Physical Quantity	Derived unit	Definition
Volume	Cubic meter	m^3
Force	Newton	$kg\text{-}m\text{-}s^{-2}$
Energy	Joule (Newton-meter)	Nm or $kg\text{-}m^2\text{-}s^{-2}$
Pressure	Pascal (Newton per square meter)	$N\text{-}m^{-2}$ or $kg\text{-}m^{-1}\text{-}s^{-2}$

It was also agreed upon that in SI units, prefixes may represent multiples or decimal fraction of various units as shown in Table 3.0.

Table 3.0. Prefixes Used in the SI and Metric System of Measurements

Prefix	**Abbreviation**	**Meaning**
Peta	P	10^{15}
Tera	T	10^{12}
Giga	G	10^{9}
Mega	M	10^{6}
Kilo	k	10^{3}
Deci	d	10^{-1}
Centi	c	10^{-2}
Milli	m	10^{-3}
Micro	µ	10^{-6}
Nano	n	10^{-9}
Pico	p	10^{-12}
Femto	f	10^{-15}
Atto	a	10^{-18}
Zepto	z	10^{-21}

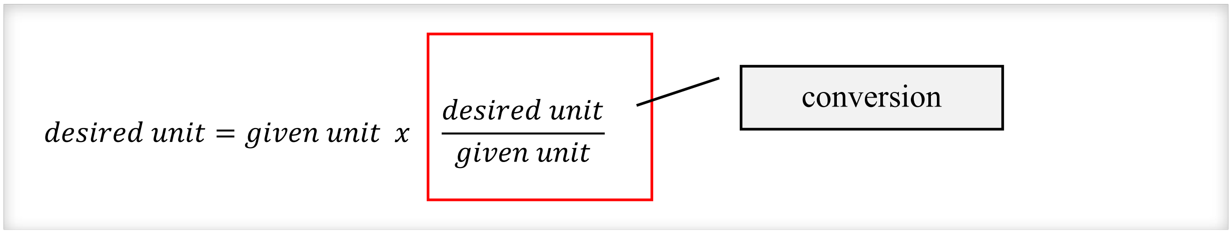
There are different system of units available and are being used in different communities around the world. The common ones are as shown in Table 4.0.

Table 4.0. Common Systems of Measurements

Physical Quantities		**Systems of Measurement**		
	SI	**Metric**	**CGS**	**English**
Mass	Kilogram	Kilogram	gram	Pound
Length	Meter	Meter	centimeter	Foot
Time	Second	Second	second	Second

Temperature	Kelvin	Kelvin	Kelvin	Rankine
Amount of Substance	Mole	Mole	mole	Pound-mole
Volume	cubic meter	liter	centiliter	gallon
Force	Newton	Newton		Pound-force
Energy	Joule	Joule	Ergs	Foot-pound-force
Pressure	Pascal	Pascal		Pound per square inch

Due to the existence of the different systems, a skill on converting one unit to the other is needed in order to solve problems on thermodynamics. Such skill is known as **dimensional analysis** (Figure 1.0.) wherein one uses conversion factors to jump from one unit to another. **Conversion factors** are fractions composed of a numerator and a denominator of the same magnitude expressed in different units as shown in Table 5.0.



$$desired\ unit = given\ unit\ x\ \boxed{\frac{desired\ unit}{given\ unit}}$$

Figure 1.0: The process of dimensional analysis

Table 5.0 Common Conversion Factors

Quantity	**Conversion**
Mass	1 kg = 10^3 g = 2.2046 lb 1 lb = 453.59 g = 16 oz
Length	1 m = 100 cm = 3.28084 ft = 39.3701 in = 1.0936 yd 1 km = 0.62137 mi 1 mi = 5280 ft = 1.6093 km 1 in = 2.54 cm
Volume	1 m^3 = 10^6 cm^3 = 35.3147 ft^3 = 264.172 gal 1 L = 10^{-3} m^3 = 1 dm^3 = 10^3 cm^3 = 1.0567 qt 1 gal = 4 qt = 3.7854 L 1 cm^3 = 1 mL

Force	1 N = 1 kg m s^{-2} = 10^5 dyne = 0.224 lb_f
Energy	1 J = 1 kg m^2 s^{-2} = 1 N m = 1 m^3 Pa = 10^{-5} m^3 bar = 10 cm^3 bar = 9.86923 cm^3 atm = 10^7 dyne cm = 10^7 erg = 0. 239006 cal = 5.12197 x10^{-3} ft^3 psia = 0.737562 ft lb_f = 9.47831 x10^{-4} Btu = 1 C-V 1 cal = 4.184 J 1 eV = 1.602 x10^{-19} J
Pressure	1 bar = 10^5 kg m^{-1} s^{-2} = 10^5 N m^{-2} = 10^5 Pa = 10^6 dyne cm^{-2} = 0.986 atm = 14.5038 psia = 750.061 torr 1 Pa = 1 N m^{-2} = 1 kg m s^{-2} 1 atm = 1.01325 x10^5 Pa = 760 torr = 14.7 psi 1 torr = 1 mmHg
Power	1 kW = 10^3 W = 10^3 J s^{-1} = 239.006 cal s^{-1} = 737.562 ft lb_f s^{-1} = 0.947831 BTU s^{-1} = 1.34102 hp
Temperature	K = °C + 273.15 °C = 5/9 (°F -32°)

Measures on the Amount or Size

Mass is a measure of the amount of matter in an object.

Weight of an object is the force acting on it due to gravitational force.

Volume is the amount of space that is occupied by a substance.

Molar volume is the volume is the one mole of a substance.

Density of a substance is the ratio of the mass to the volume of the substance.

Specific volume of a substance is the ratio of the volume to the mass of the substance.

Specific weight of a substance is the ratio of the weight to the volume of a substance.

Specific gravity (relative density) of a liquid is the ratio of density of the liquid to the density of water at a specified temperature.

Specific gravity (relative density) of a gas is the ratio of the density of air to the density of water at a specified temperature and pressure.

Temperature

Temperature is the measure of the coldness or warmth of a substance.

Absolute temperature is the temperature measured using a scale beginning at zero, with that zero being the coldest theoretically attainable in nature.

Boiling point – the state wherein the liquid and the gaseous phases of a substance is at equilibrium.

Melting point – the state wherein the solid and the liquid phases of a substance is at equilibrium.

Triple point – the state wherein all three phases (solid, liquid and gas) of a substance coexist simultaneously (Triple point of water is 0.01°C)

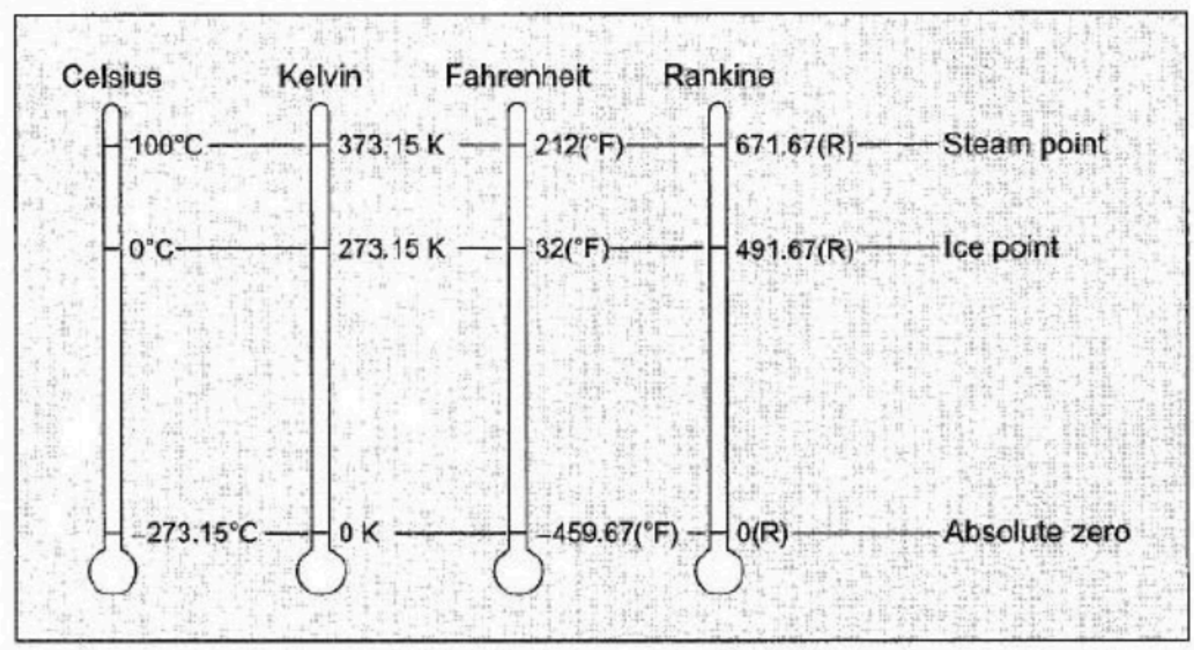


Figure 1: Relationship among different temperature scales.

Derivation of formula on the conversion of one temperature scale to another:

Working principle: A substance has the same interval from its ice to the steam points regardless of the scale.

a. K = °C + 273.15

Steam Point	373.15	100°
Temperature scale	K	°C
Ice Point	273.15	0°

$$\frac{373.15 - 273.15}{K - 273.15} = \frac{100 - 0}{℃ - 0}$$

$$\frac{100}{K - 273.15} = \frac{100}{℃}$$

$$K = ℃ + 273.15$$

b. °C = 5/9 (°F -32°)

Steam Point	100°	212°
Temperature scale	°C	°F
Ice Point	0°	32°

$$\frac{100 - 0}{℃ - 0} = \frac{212 - 32}{℉ - 32}$$

$$\frac{100}{℃} = \frac{180}{℉ - 32}$$

$$\frac{5}{℃} = \frac{9}{℉ - 32}$$

$$℃ = \frac{5}{9}\,(℉ - 32)$$

Pressure

Pressure is defined as the amount of the normal force that is exerted over a specific surface area.

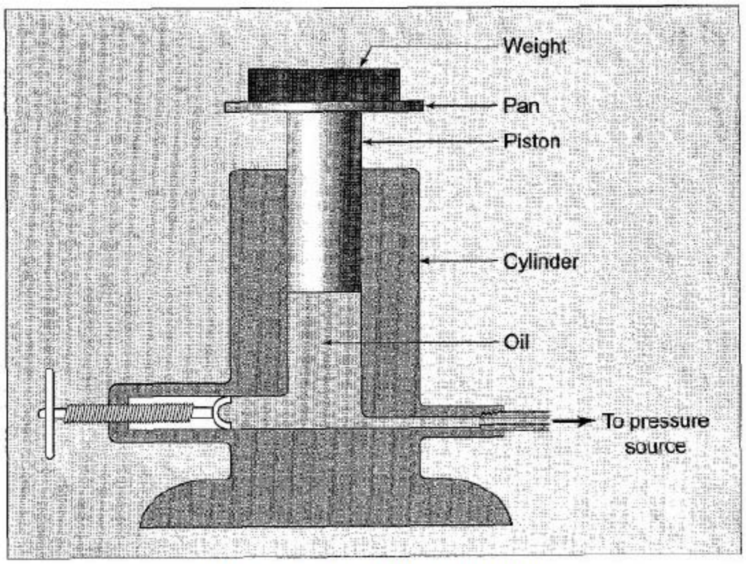


Figure 2: Dead-weight gauge

__Derivation of formulas used for calculations of pressure exerted by a fluid over a surface area:__

Let P = pressure exerted by the fluid
F = normal force exerted by the fluid
A = surface area on which the force is exerted to
m = mass of the fluid
g = gravitational acceleration exerted on the fluid
V = volume of the fluid
ρ = density of the fluid
h = height difference of the fluid resulting from the exerted force

From the definition of pressure,

$$Pressure, P = \frac{Force, F}{Area, A}$$

$$\boldsymbol{P = \frac{F}{A}}$$

But Force is the product of mass, m and gravitational acceleration,g

$$P = \frac{m\,g}{A}$$

But density, ρ is defined as the ratio of the mass (m) over volume (V) of the fluid,

$$P = \frac{\rho\, V\, g}{A}$$

But Volume is the product cross-sectional area, A and height of the fluid, h

$$P = \frac{\rho\, A\, h\, g}{A}$$

$$\boldsymbol{P = \rho\, h\, g}$$

Therefore, the pressure that is inserted by the fluid is the product of the fluid density, the height difference resulting from the pressure and the gravitational acceleration.

Atmospheric pressure (Pressure$_{atm}$) is the pressure that is exerted by the atmosphere.

Gauge pressure (Pressure$_{gauge}$) is the pressure at a point in a fluid above that of the atmosphere.

Absolute pressure (Pressure$_{abs}$) is a pressure that is relative to the zero pressure in the empty, air-free space of the universe.

$$Pressure_{absolute} = Pressure_{atmospheric} + Pressure_{\,gauge}$$

Sample Problem 01:

Carry out the following conversions of energy units: (a) 14.3 BTU into cal, (b) 1.4 x10^5 cal into joules, (c) 31.6 mJ into BTU

Solution:

$$\text{Energy, cal} = 14.3\; BTU \times \frac{0.239006\; cal}{9.47831\; x10^{-4} BTU} = 3.61\; x\; 10^2\; cal$$

$$Energy, J = 1.4\; x10^5\; cal \times \frac{1\, J}{0.239006\; cal} = 5.9\; x10^6\; J$$

$$Energy, BTU = 31.6\; mJ \times \frac{1\, J}{1000\; mJ} \times \frac{9.47831\; x10^{-4}}{1\, J} = 3.00\; x10^{\,-5}\; BTU$$

Sample Problem 02:

Make the following conversions: (a) 72°F to °C; (b) 216°C to °F; (c) 233°C to K; (d) 315K to °F; (e) 0K to °F

Solution:

$$Temperature, ℃ = \frac{5}{9}\,(℉ - 32) = \frac{5}{9}\,(72 - 32) = 22\; ℃$$

$$Temperature, {}^{\circ}\mathrm{F} = \frac{9}{5}{}^{\circ}\mathrm{C} + 32 = \left[\left(\frac{9}{5}\right)(216)\right] + 32 = 421\ {}^{\circ}\mathrm{F}$$

$$Temperature, K = {}^{\circ}\mathrm{C} + 273.15 = 233 + 273.15 = 506.15\ K$$

$$Temperature, {}^{\circ}\mathrm{F} = \left[\frac{9}{5}(K - 273.15)\right] + 32 = \left[\frac{9}{5}\ (315 - 273.15)\right] + 32 = 107.33\ K$$

$$Temperature, {}^{\circ}\mathrm{F} = \left[\frac{9}{5}\ (K - 273.15)\right] + 32 = \left[\frac{9}{5}\ (315 - 0)\right] + 32 = 599\ {}^{\circ}\mathrm{F}$$

Sample Problem 03:

Suppose you decide to define your own temperature scale using the freezing point (13°C) and boiling point (360°C) of oleic acid, the main component of olive oil. If you set the freezing point of oleic acid as 0°O and the boiling point as 100°O, what is the freezing point and boiling point of water on this new scale?

Solution:

Steam Point	360°	100°
Temperature scale	°C	°O
Ice Point	13°	0°

$$\frac{360 - 13}{{}^{\circ}\mathrm{C} - 13} = \frac{100 - 0}{{}^{\circ}O - 0}$$

$${}^{\circ}O = \frac{100}{347}\ ({}^{\circ}\mathrm{C} - 13)$$

Substitute the freezing point of water (0°C) to the derived equation:

$$Freezing\ point, {}^{\circ}O = \frac{100}{347}\ (0 - 13) = \ -3.75\ {}^{\circ}O$$

Substitute the boiling point of water (100°C) to the derived equation:

$$Boiling\ point, {}^{\circ}O = \frac{100}{347}(100 - 13) = 25.1\ {}^{\circ}O$$

Sample Problem 04:

The density of air at ordinary atmospheric pressure and 25°C is 1.19 g/L. What is the mass, in kilograms, of the air in a room that measures 14.5 ft x 16.5 ft x 8.0 ft.

Given: Density of air = 1.19 g/L
Rectangular room dimension = 14.5 ft x 16.5 ft x 8.0 ft.

Required: mass of air
Solution:

From the definition of density,

$$density, \rho = \frac{mass, m}{volume, V}$$

Rearranging the equation will lead to the working formula,

$$mass, m = \ (density, \rho)\ x\ volume, V$$

Take note that the volume of a rectangle is length x width x height,

$$mass, m = density\ x\ length\ x\ weight\ x\ height$$

Substituting the given values,

$$mass = \left(\frac{1.19\ g}{L}\right)(14.5\ ft)(16.5\ ft)(8.0\ ft)\left(\frac{12\ in}{1\ ft}\right)^3\left(\frac{2.54\ cm}{1\ in}\right)^3\left(\frac{1\ mL}{1\ cm^3}\right)\left(\frac{1\ L}{1000\ mL}\right)\left(\frac{1\ kg}{1000\ g}\right)$$

$$mass = 64.5\ kg$$

Sample Problem 05:

A sample of tetrachloroethylene, a liquid used in dry cleaning that is being phased out because of its potential to cause cancer, has a mass of 40.55 g and a volume of 25.0mL at 25°C. What is its density at this temperature? (b) Carbon dioxide is a gas at room temperature and pressure. However, carbon dioxide can be put under pressure to become supercritical fluid that is much safer dry-cleaning agent than tetrachloroethylene. At a certain pressure, the density of supercritical CO_2 is 0.469 g/cm^3. What is the mass of a 25.0mL sample of supercritical CO_2 at this pressure?

a) Given: Carbon tetrachloride
Mass = 40.55 grams
Volume = 25.0 mL
Required: density of carbon tetrachloride
Solution:

$$density, \rho = \frac{mass, m}{volume, V} = \frac{40.55\ grams}{25.0\ mL} = 1.622\ \frac{g}{mL}$$

b) Given: Carbon dioxide
Density = 0.469 g/cm^3
Volume = 25.0 mL

Required: mass of carbon dioxide
Solution:

$$mass, m = \ (density, \rho)(volume, V) = \ \left(0.469\ \frac{g}{cm^3}\right)(25.0\ mL)\left(\frac{cm^3}{mL}\right) = 11.7\ g$$

Sample Problem 06:

An astronaut weighs 739N in Houston, Texas, where the local acceleration of gravity is g = 9.793 m/s^2. What are the astronaut's mass and weight in the moon where g = 1.67 m/s^2?

Solution:

Given:

	Texas	Moon
Mass	(?)	(?)
Gravitational acceleration	9.793 m/s^2	1.67 m/s^2
Weight	739 Newtons	(?)

Required: The mass and weight of the man in the moon

Solution:

$$Force = mass\ x\ \ gravitaitonal\ acceleration$$

$$mass = \frac{Force}{gravitational\ acceleration}$$

Calculating for the mass of the man in Texas,

$$mass_{Texas} = \frac{Weight_{Texas}}{gravitational\ acceleration_{Texas}} = \left(\frac{739\ N}{9.793\ \frac{m}{s^2}}\right)\left(\frac{1\ \frac{kg\ m}{s^2}}{1\ N}\right) = 75.5\ kg$$

Calculating for the mass of the man in the moon,

$$mass_{Moon} = mass_{Texas} = 75.5\ kg$$

Calculating for the weight of the man in the moon,

$$weight_{Moon} = \ (mass_{Moon})(gravitational\ accelration_{moon})$$

$$weight_{moon} = \ (75.5\ kg)\left(1.67\frac{m}{s^2}\right)\left(\frac{1\ N}{1\ \frac{kg\ m}{s^2}}\right) = 126\ N$$

Sample Problem 07:

A dead-weight gauge with a 1-cm diameter piston is used to measure pressures very accurately. In a particular instance, a mass of 6.14kg (including piston and pan) brings it into balance. If the local acceleration of gravity is 9.82 m/s^2, what is the gauge pressure being measured? If the barometric pressure is 748 torr, what is the absolute pressure?

Given: dead-weight gauge,
diameter = 1 cm
mass = 6.14 kg
gravitational acceleration, g = 9.82 m/s^2

Required: Gauge pressure and absolute pressure when the barometric pressure is 748 torr
Solution:

Solving for the gauge pressure,

$$Pressure_{guage} = \frac{Force}{Area} = \frac{mass\ x\ gravitational\ acceleration}{Area_{circle}}$$

$$Pressure_{guage} = \frac{(6.14\ kg)\left(9.82\ \frac{m}{s^2}\right)}{\left[\frac{\pi}{4}\ (1\ cm)^2\right]\left(\frac{1\ m}{100\ cm}\right)^2}\left(\frac{1\ N}{1\ \frac{kg\ m}{s^2}}\right)\left(1\ \frac{1\ Pa}{N/_{m^2}}\right)\left(\frac{1\ kPa}{1000\ Pa}\right) = 768\ kPa$$

Solving for the absolute pressure,

$$Pressure_{absolute} = Pressure_{guage} + Pressure_{barometric}$$

$$Pressure_{absolute} = 768\ kPa + \left[(748\ torr)\left(\frac{1\ atm}{760\ torr}\right)\frac{101.325\ kPa}{1\ atm}\right] = 867\ kPa$$

Sample Problem 08:

At 27°C, the reading on a manometer filled with mercury is 60.5 cm. The local acceleration of gravity is 9.784 m/s^2. To what pressure does this height of mercury correspond? Express answer in bar. Density of mercury at 27°C is 13.53 g/cm^3.

Given: mercury manometer reading = 60.5 cm
Gravitational acceleration = 9.784 m/s^2
Density of mercury = 13.53 g/cm^3

Required: Pressure

Solution:

$$Pressure = density\ of\ the\ fluid\ x\ height\ of\ the\ fluid\ x\ gravitational\ acceleration$$

$$Pressure = \left(13.53\ \frac{g}{cm^3}\right)(60.5\ cm)\left(9.784\ \frac{m}{s^2}\right)\left(\frac{1\ N}{1\ \frac{kg\ m}{s^2}}\right)\left(\frac{100\ cm}{1\ m}\right)^2\left(\frac{1\ Pa}{N/_{m^2}}\right)\left(\frac{1\ bar}{1\ x\ 10^5\ Pa}\right)$$

$$Pressure = 0.801\ bar$$

Sample Problem 09:

A fluid has a density of 920 kg/m^3. What is the specific gravity of the fluid?

Given: fluid density = 920 kg/m^3
Required: fluid specific gravity
Solution:

$$Specific\ Gravity = \frac{fluid\ density, \rho_L}{water\ density, \rho_{H_2O}} = \frac{920\ \frac{kg}{m^3}}{1000\ \frac{kg}{m^3}} = 0.92$$

Sample Problem 10:

A condenser vacuum gauge read 580 mmHg when the barometer reads 760 mmHg. Determine the absolute condenser pressure in bars.

Given: Vacuum gauge reading = 580 mmHg
Barometer reading = 760 mmHg

Required: Absolute pressure in bars

Solution:

$$Pressure_{absolute} = Pressure_{gauge} + Pressure_{barometric}$$

$$Pressure_{absolute} = (-580\ mmHg + 760\ mmHg)\left(\frac{1\ atm}{760\ mmHg}\right)\left(\frac{1.01325\ x10^5\ Pa}{1\ atm}\right)\left(\frac{1\ bar}{1\ x10^5\ Pa}\right)$$

$$Pressure_{absolute} = \mathbf{0.24}\ bar$$

Activities and Assessments:

1.) Derive a formula that can be used to convert a temperature reading from Kelvin to Rankine scales.
2.) 5. An Olympic-size pool is 50.0 m long ang 25.0 m wide. How many gallons of water (density = 1.0 g/mL) are needed to fill the pool to an average depth of 4.8 ft?
3.) An iron block weighs 5N and has a volume of 200 cm^3. What is the density of the block in kg/m^3?

4.) The equivalent pressure gauge of a compound gauge measuring a pressure of 25.3 inches mercury is ____. Density of mercury is 13.53 g/cm^3: Express your answer in kilopascal.
5.) A 15cm diameter piston was uniformly applied by a force of 1200 N. Find the pressure on the piston. Express answer in kilopascals.

LESSON 03: THERMODYNAMIC CONCEPTS
Unit 02: Understanding the World of Thermodynamics

INTRODUCTION:

The relationship of chemical energy and thermodynamics was established in the previous section. In order to harness the energies stored in fuels a better understanding of the concepts of thermodynamics is needed to be established first. However, thermodynamics is a world that speaks of its own language. Understanding the world of thermodynamics means getting used to its unique language.

LESSON OBJECTIVES:

After successful completion of this lesson, the students are expected to:

1.) Define and give examples of the different classifications of a system.
2.) Define and give examples of extensive and intensive properties.
3.) Define what is a state function.
4.) Define and differentiate the different thermodynamic processes.

COURSE MATERIALS:

What is Thermodynamics?

Thermodynamics is the study of the interrelationships among various forms of energy. It comes from the Greek words “therme” (heat) and “dy’namis” (power), which literary means “power from heat”.

Chemical thermodynamics, on the other hand, is a branch of thermodynamics that deals with the relationship between heat and work from chemical reactions such as the combustion of fuel.

The Thermodynamic System

Since thermodynamics has very large scope, there is a need for the study of interest to be defined and be separated from the rest of the universe. The defined scope is known as the “**system**” and everything that is not within the system is known as the “**surroundings**”. The system and surroundings are separated by a “**boundary**” that can either be real or imaginary. (Figure 1.0)

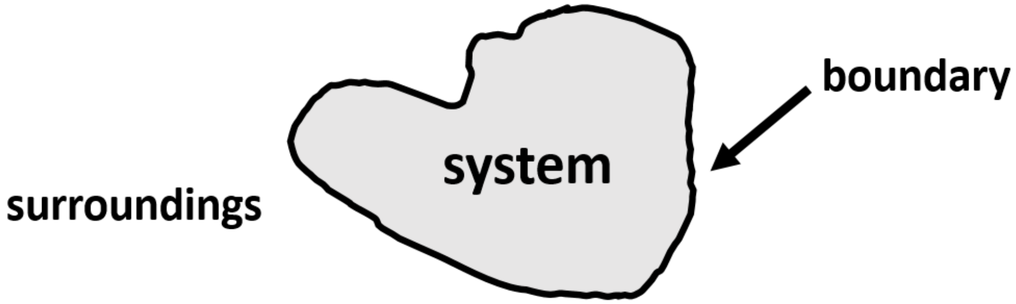


Figure 1.0: In the study of thermodynamics, it is important to separate the focus of interest, known as the system, from the rest of the universe.

Both the thermodynamic system and the surroundings has their own amount of materials and energies that can pass through the boundary. With this, a thermodynamic system can be classified as isolated, closed or open. A system is considered as **isolated** when it is not capable of exchanging both matter and energy with its surroundings such as a hot water inside a perfectly isolated thermal container. When the system is only capable of exchanging energy but not matter with its surroundings, it is classified as a **closed** system. An example of which is a hot water inside a perfectly closed container. Meanwhile, a system is classified as **open** when the system is capable of exchanging both matter and energy with its surrounding such as a pot of boiling water. Energy in the form of heat is introduced to the system to cause its boiling. After sometime, some of the water molecules escape from the system as it changes its phase from liquid to vapor.

A system can also have different phases: they can either be homogeneous or heterogeneous. P**hase** is defined as a part of a mechanically separable portion of a material with a homogeneous physical distinction. A system is considered **homogeneous** when it only consists of only one phase such as a glass of distilled water. On the other hand, a system is considered **heterogeneous** when it consists of two or more phases such as a glass of saltwater.

Thermodynamic States and Properties

A system has its own composition and energy that are both measurable. Its composition can be determined through measuring the system component's mass and volume. These measurable amounts of materials can be further used to define the amount of energy it contains by checking on the systems prevailing pressure and temperature. The composition, volume, temperature and pressure are measurable physical quantities that enables us to define the thermodynamic property of a system; hence, are considered as **thermodynamic parameters**.

The parameters that are being measured in a thermodynamic system gives its characteristic that can be quantitatively evaluated known as the system's **property**. These parameters have magnitudes that may either be dependent or independent on the amount of material being measured. A system is said to have an **intensive** property if the magnitude of the measured property is not dependent on the amount of material being measured such as temperature and density. On the other hand, a system has an **extensive** property if the magnitude of the measured property is dependent on the amount of material being measured such as volume and energy.
The system's thermodynamic parameters describes its **thermodynamic state** in a way that a change in value of one or more thermodynamic parameters can result to a change of its state. With this, the state of the system also determines its corresponding phase as can be seen on Figure 2.1.

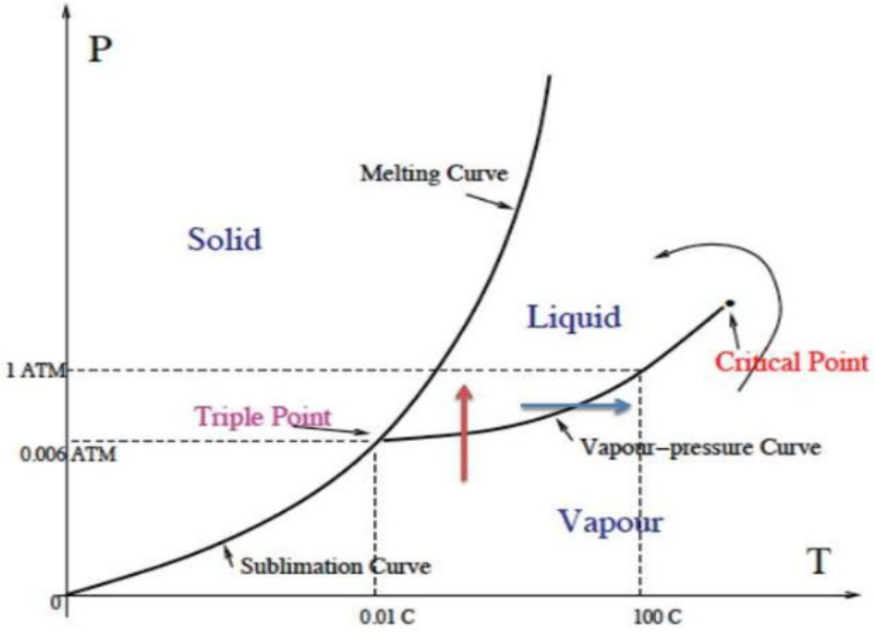


Figure 2.1. Phase Diagram of Water[1]

With variations of thermodynamic parameters, a system can undergo changes from an initial to a final state but it needs to go through some series of states called **path**. When the change of a system that occurred only depends on the state of the system but not on the path followed by the system during the change, we say that the system has a thermodynamic property known as **state function**. Most of the types of energies discussed in thermodynamics have state function properties.

Thermodynamic Processes

A **thermodynamic process** is defined as the transformation of a thermodynamic system undergoes changes from one system to another. They can be classified as flow or nonflow and reversible and irreversible processes.

A **flow process** is the one in which flow of fluid (either gas or liquid) undergoes through an open system while a **nonflow process** is the one in which fluid flow undergoes a closed system. In an open system, the amount of material in the system changes over time, while in a closed system, the flow of material is under a steady-state condition, that is, the amount of material in the system does not vary over time.

An **irreversible process** is one in which the system and the surrounding cannot go back to their original states after undergoing thermodynamic changes. Meanwhile, a **reversible process** is one which the energy change in every step of the process can be reversed in direction by an infinitesimal change in any of the variables acting on the system. A process can be made reversible by performing the change very slowly with no friction and no finite temperature differences.[2]

Thermodynamic changes occur differently depending on the changes on the different thermodynamic variables that comprise the system. There are times that some of the variables are held constant which leads to the different types of thermodynamic processes available. When a process undergoes changes under a constant temperature, it is called an **isothermal process**.

When a process undergoes changes under a constant pressure, it is called an **isobaric process**. When a process undergoes changes under constant volume, it is called an **isochoric process**. Whenever changes in a temperature in a system occur but there is no heat flow exchanged between the system and surroundings involved, the process is known to be **adiabatic**.

Activities and Assessments:

1.) Give an example each of an isolated, closed and an open systems. Explain how you classified the systems.
2.) Give two (2) examples each of intensive and extensive properties of a system.
3.) In your own words, define state function.
4.) State the Boyle's Law on ideal gases. What kind of thermodynamic process did the gas underwent when Boyle conducted the experiment?

LESSON 04: THERMOCHEMISTRY
Unit 01: The First Law of Thermodynamics

Introduction:

Thermochemistry the branch of thermodynamics that deals with the thermal changes accompanying chemical and physical transformations. It aims include the (1) determination of the quantities of energy emitted or absorbed as heat in various processes and (2) the development of methods for calculating thermal readjustments without recourse of experiment. The underlying principles behind thermochemistry is the First Law of Thermodynamics; hence, before diving in into thermochemistry, it is important to learn first the concepts behind the Law of Conservation to Enrgy.

Lesson Objectives:

After successful completion of this lesson, the students are expected to:

1.) Interpret the First Law of Thermodynamics into its different forms of statements including its correct mathematical formulation.
2.) Describe the concept and importance of the Joule's experiment.
3.) Demonstrate the understanding of internal energy concepts and its relationship to heat and work.
4.) Solve problems on PV-work of a system.
5.) Demonstrate the understanding on the concept of enthalpy through problem solving activities.

Course Materials:

The First Law of Thermodynamics

The First Law of Thermodynamics is also known as the Law of Conservation of Energy.

"The energy of an isolated system remains constant and whenever a quantity of some form of energy disappears, an exactly equivalent quantity of some other form of energy must make its appearance."

$$\Delta(Energy\ of\ the\ system) + \Delta(Energy\ of\ the\ surroundings) = 0$$

Joule's Experiment

English scientist James Prescott Joule conducted an experiment that became one of the great foundations of thermodynamics; hence, named after him.

A known amount of water was placed in an insulated container and was agitated with a rotating stirrer. Both of the work done on the water and the temperature changes were recorded. It was found out (1) that a fixed amount of work was required per unit mass of water for every degree of temperature rise caused by the stirring and (2) that the original temperature of water could be restored by the transfer of heat through simple contact with a cooler object. Through the experiment, it was shown that (1) there is a quantitative relationship existing between work and heat and (2) heat is a form of energy.

In the Joule's Experiment, energy is added to the water as work but is extracted from the water as heat. What happened to the energy between the time it was added to the water as work and the time it was extracted as heat is believed to be contained in the water in another form of energy, defined as internal energy.

Internal Energy, U

Internal energy is the energy that is found within the system itself and is a function of temperature, chemical composition, volume and pressure of the system. Its magnitude refers to the total energy of the molecules that comprises the system.

$$\Delta U = U_{final} - U_{initial}$$

When dealing with internal energy, there are important notes that are needed to be considered:

1. Internal energy has a fixed value for a given sets of conditions.
2. The conditions that influence internal energy are temperature and pressure.
3. The internal energy of a system is proportional to the total quantity of matter in the system because energy is an extensive property.
4. Internal energy is a state function.

The Mathematical Formulation of the First Law

The change in internal energy of a system is the sum of the heat (Q) transferred to the system and the work (W) done on the system.

$$\Delta \boldsymbol{U} = \boldsymbol{Q} + \boldsymbol{W}$$

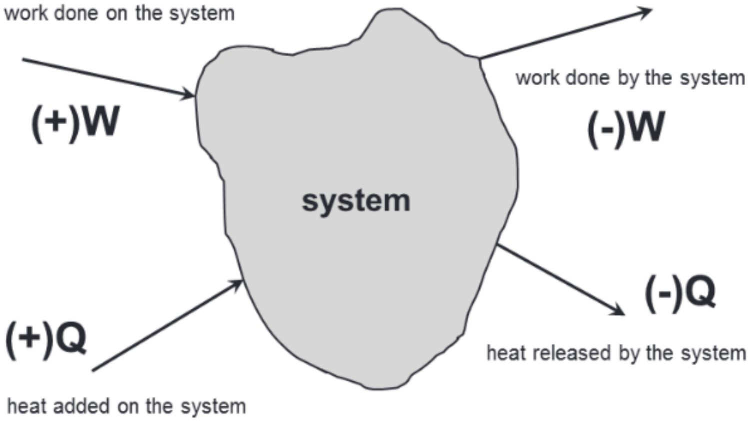


Figure 1: Sign convention for heat and work.

Endothermic process – a process wherein the system absorbs heat from the surrounding. The heat flows into the system.

Exothermic process – a process wherein the system releases heat to the surrounding. The heat exists and flows out of the system.

For a system that absorbs heat and does work to the surroundings: $\Delta E = Q - W$

For cyclic process, $Q = W$ because there is the final and initial energies of the system are the same, $\Delta E = 0$

For adiabatic process = $W = -\Delta E$ because for an adiabatic process $Q = 0$

Sample Problem 1:

Calculate the change in internal energy for a process in which the system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings.

Given: $Q = 140$ J
$W = -85$ J

Required: ΔU

Solution:

$$\Delta U = Q + W$$

$$\Delta U = 140\,J + (-85\,J) = 55\,J$$

Answer: $\Delta U = 55$ J

Sample Problem 2:

Calculate ΔU and determine whether the process is endothermic or exothermic for the following cases:

(a) $Q = 0.763$ kJ and $W = -840$ J
(b) a system releases 66.1 kJ of heat to its surroundings while the surroundings do 44.0 kJ of work on the system

Given: $Q = 140$ J
$W = -85$ J

Required: ΔU, process qualification

Solution:

$$\Delta U = Q + W$$

$$\Delta U = 140\ kJ - \left[840\ J \times \frac{1\ kJ}{1000\ J}\right] = -0.077\ kJ$$

Answer: ∆U = - 0.077 kJ; Q is (+); therefore, the process is endothermic

Given: $Q = -66.1$ kJ
$W = 44.0$ kJ

Required: ∆U, process qualification

Solution:

$$\Delta U = Q + W$$
$$\Delta U = -66.1\ kJ + 44.0\ kJ = -22.1\ kJ$$

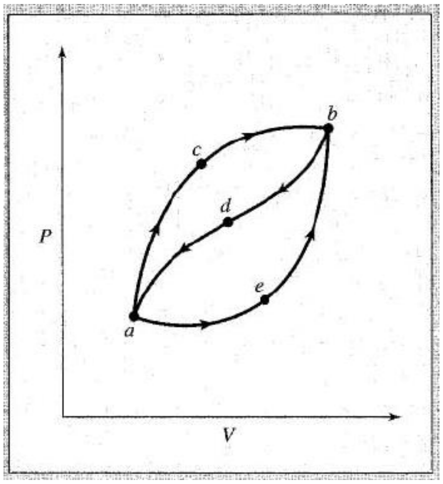
Answer: ∆U = - 22.1 kJ; Q is (-); therefore, the process is exothermic.

Sample Problem 3:

When a system is taken from state a to b, as shown in the figure, along path acb, 100J of heat flows into the system and the system does 40J of work.

(a) How much heat flows into the system along path aeb if the work done by the system is 20J?

(b) The system returns from b to a along path bda. If the work done on the system is 30J, does the system absorb or liberate heat?



Given: $Q_{acb} = 100$ J
$W_{acb} = -40$ J
$W_{aeb} = -20$ J

Required: Q_{aeb}

Solution:

$$\Delta U_{acb} = Q_{acb} + W_{acb}$$

$$\Delta U_{acb} = 100\ J - 40\ J = 60\ J$$

Since internal energy is a state function,

$$\Delta U_{aeb} = \Delta U_{acb} = 60\ J$$

$$\Delta U_{aeb} = Q_{aeb} + W_{aeb}$$

$$Q_{aeb} = \Delta U_{aeb} - W_{aeb}$$

$$Q_{aeb} = 60\,J - (-20\,J) = 80\,J$$

Answer: Q_{aeb} = 80 J

Given: Q_{acb} = 100 J
W_{acb} = - 40 J
W_{bda} = 30 J

Required: Does Qbda absorb or liberate heat?

Solution:

$$\Delta U_{bda} = -\Delta U_{bca} = -\Delta U_{aeb} = -60\,J$$

$$\Delta U_{bda} = Q_{bda} + W_{bda}$$

$$Q_{bda} = \Delta U_{bda} - W_{bda}$$

$$Q_{bda} = -60\,J - 30\,J = -90\,J$$

The PV-work System

The PV work is the work that results to an expansion or contraction of a system.

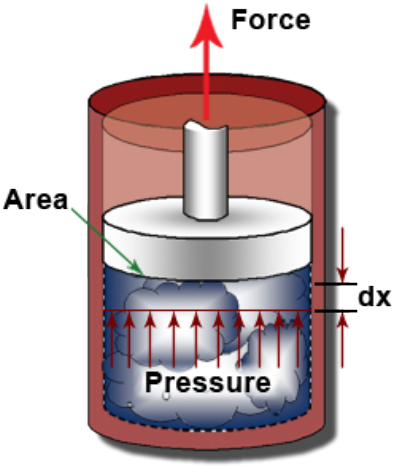


Figure 3: An illustration in the PV work. Image source: www.learnthermo.com

Imagine a gas contained inside a cylinder with a moveable piston as shown in Figure 3. The changing pressure of the gas, creates force that result for the piston to rise at a certain distance (dx). This change in distance also changed the volume of the gas. Given the definition of work and the situation, it can be said that the gas did an expansion work on the piston.

Work is defined by the force (F) to cause a displacement (dx)

$$dW = F \times dx$$

Pressure (P) is defined as the normal force (F) acting on a surface of a specific area (A)

$$P = \frac{F}{A}$$

Substituting the definition of pressure to the work equation,

$$dW = P\ A\ dx$$

The change in distance caused by the expansion of the gas caused a change in the volume of the gas,

$$dV = A\ dx$$

Substituting the dV equation to the dW equation,

$$dW = P\ A\ \frac{dV}{A}$$

$$\int dW = P \int_{V_1}^{V_2} dV$$

$$W = P\ dV$$

Expansion and Contraction PV works

In the above derivation for the formula of PV-work, the gas is considered as the system. However, the conventions on the mathematical formulation of the First Law of Thermodynamics was not considered; hence, is needed to be checked.

For expansion:	For contraction:
The volume of the gas was increased; therefore, $V_1 < V_2$	The volume of the gas was increased; therefore, $V_1 > V_2$
Substituting the values of V1 and V2 to the work equation will result in a positive (+) value of W.	Substituting the values of V1 and V2 to the work equation will result in a positive (-) value of W.
BUT	BUT
Work is done by the gas to the piston; hence, the sign of W should be negative (-), following the convention for work.	Work is done by piston on the gas; hence, the sign of W should be negative (+) following the convention for work.

Given the above scenarios on the inconsistencies of the signs of the PV-work with the convention on the sign of W that was initially established, a correction on the derived formula is incorporated:

$$\boldsymbol{W = -P\int_{V_1}^{V_2} dV}$$

Reversible and Irreversible PV works

Reversible process is one in which the energy change in every step of the process can be reversed in direction by an infinitesimal change in any of the variables acting on the system. A process can be made reversible by performing the change very slowly with no friction and no finite temperature differences.

Irreversible process is one in which the system and the surrounding after undergoing changes cannot get back to their initial state and tend to proceed to a different direction but cannot proceed to the reverse direction.

Isothermal processes in ideal gases

Work done by a gas against a constant pressure and temperature,

$$W_{ig} = -P\,(V_2 - V_1)$$

Work done by a gas undergoing isothermal and reversible expansion,

$$W_{ig} = -P\int_{V_1}^{V_2} dV = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -(nRT)\left(\ln\frac{V_2}{V_1}\right) = (nRT)\left(\ln\frac{V_1}{V_2}\right)$$

Sample Problem 4:

Find the work done when 2 moles of hydrogen expand isothermally from 15 to 50 liters against a constant pressure of 1 atm at 25°C. Express answer in calorie.

Given: 2 moles H_2
Isothermal expansion
$V_1 = 15$ L
$V_2 = 50$ L
P = 1 atm
T = 25°C

Required: Work done by the ideal gas, in calories

Solution:

$$W_{ig} = P\,(V_2 - V_1)$$

$$W_{ig} = (1\ atm)(50\ L - 15\ L)\left(\frac{24.22\ cal}{1\ L - atm}\right) = 848\ cal$$

Answer: Work done by the ideal gas is 848 calories.

Sample Problem 5:

Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 15 to 50 liters. Express answer in calorie.

Given: 2 moles H_2
Isothermal and reversible expansion
$V_1 = 15$ L
$V_2 = 50$ L
T = 25°C

Required: Work done by the ideal gas, in calories

Solution:

$$W_{ig} = nrt\left(\ln\frac{V_1}{V_2}\right) = (2\,mol)\left(0.08205\,\frac{L-atm}{mol-K}\right)(25℃ + 273.15)\left(\ln\frac{15\,L}{50\,L}\right)\left(\frac{24.22\,cal}{1\,L-atm}\right)$$
$$= -\,1427\,cal$$

Answer: Work done by the ideal gas is 1427 calories.

Sample Problem 6:

A gas is confined in a cylinder by a piston. The initial pressure of the gas is 7 bars and the volume is $0.10m^3$. The piston is held in place by latches in the cylinder wall. The whole apparatus is placed in a total vacuum. What is the energy change of the apparatus if the retaining latches are removed so that the gas suddenly expands to double its initial volume? The piston is again held by latches at the end of the process.

Given: P_{gas} = 7 bars
V_{gas} = 0.10 m^3
Gas is inside a piston-cylinder system that was placed inside a vacuum.

Required: ΔU

Solution:

$$\Delta U = Q + W$$

The system is the whole apparatus comprising of the gas, the piston and the cylinder.
Q = 0, there is no heat transfer to and from the apparatus because of the presence of the vacuum.
W = 0, there no work done during the process because there is no external force to the system because of the vacuum.

Answer: ΔU is zero.

Sample Problem 7:

If the process described in the previous problem is repeated, not in a vacuum but in air at standard atmospheric pressure of 101.3 kPa, what is the energy change of the apparatus? Assume that the rate of heat exchange between the apparatus and the surrounding air to be slow compared with the rate at which the process occurs.

Given: P_{gas} = 7 bars
V_{gas} = 0.10 m^3
Gas is inside a piston-cylinder system expanding to double its volume against an atmospheric pressure of 101.3 kPa.
$V_2 = 2V_1 = 2 \times 0.10\ m^3 = 0.20\ m^3$

Required: ΔU

Solution:

$$\Delta U = Q + W$$

$$\Delta U = Q - P\int_{V_1}^{V_2} dV$$

$$\Delta U = 0 - \left[101.3\ kPa \times \frac{1000\ Pa}{1\ kPa} \times \frac{1\ {}^{N}\!/_{m^2}}{1\ Pa}\right][0.2\ m^3 - 0.1m^3]\left[\frac{1\ J}{1\ N\ m}\right]\left[\frac{1\ kJ}{1000\ J}\right] = -10.13\ kJ$$

Q = 0 because it was mentioned in the problem that “the rate of heat exchange between the apparatus and the surrounding air to be slow compared with the rate at which the process occurs” is assumed.

Answer: ΔU is –10.13 kJ.

Sample Problem 8:

The initial pressure and volume in a piston-cylinder arrangement are 300 kPa and $2m^3$, respectively. Energy is added to the system and the piston is withdrawn in such a way that the quantity PV remains constant. If the final pressure is 100 kPa, find the work done by the gas on the piston.

Given: $P_{initial}$ = 300 kPa
$V_1 = 2m^3$
PV is constant throughout the process
P_{final} = 100 kPa

Required: Work done by the gas on the piston

Solution:

$$W = -P\int_{V_1}^{V_2} dV$$

But PV = constant, k

$$P = \frac{k}{V}$$

$$W = -k \int_{V_1}^{V_2} \frac{dV}{V} = -k\ In\ \frac{V_2}{V_1}$$

Solving for k,

$$k = P_1V_1 = (300\ kPa)(2\ m^3)\left(\frac{1000\ Pa}{1\ kPa}\right)\left(\frac{1\ {}^{N}/_{m^2}}{1\ Pa}\right)\left(\frac{1\ J}{1\ N\ m}\right) = 600000\ J$$

Solving for V_2,

$$k = P_2V_2$$

$$V_2 = \frac{k}{P_2} = \frac{P_1V_1}{P_2} = \frac{(300\ kPa)(2m^3)}{100\ kPa} = 6m^3$$

$$W = -600000\ J\left[\ln\frac{6\ m^3}{2m^3}\right]\left[\frac{1\ kJ}{1000\ J}\right] = -\ 659\ J$$

Answer: The work done by the gas on the piston is 659 Joules.

Sample Problem 9:

A horizontal piston/cylinder arrangement is placed in a constant-temperature bath. The piston slides in the cylinder with negligible friction and an external force holds it on place against an initial gas pressure of 14 bar. The initial gas volume is 0.03 m^3. The external force on the piston is reduce gradually, allowing the gas to expand until its volume doubles. Experiment shows that under these conditions, the volume of the gas is related to its pressure in such a way that the product PV is constant. Calculate the work done by the gas moving the external force. How much work would be done if the external force were suddenly reduced to half its initial value instead of being gradually reduced? What is the process efficiency?

Given: piston/cylinder bath in an isothermal process (constant temperature)
Negligible friction process, a clue to reversibility
P_1 = 14 bar
V_1 = 0.03 m^3
V_2 = $2V_1$ = 0.06 m3, double it volume
PV = constant

Required:
(a) work done by the gas (reversible)
(b) work done by the gas (irreversible)
(c) process efficiency

Solution:

(a) work done by the gas (reversible)

$$W = -P\int_{V_1}^{V_2} dV$$

But PV = constant, k

$$P = \frac{k}{V}$$

$$W = -k\int_{V_1}^{V_2}\frac{dV}{V} = -k\; In\;\frac{V_2}{V_1}$$

Solving for k,

$$k = P_1V_1 = (14\; bar)(0.03m^3)\left(\frac{1\; x\; 10^5\; Pa}{1\; bar}\right)\left(\frac{1\; {}^{N}\!/_{m^2}}{1\; Pa}\right)\left(\frac{1\,J}{1\; N\; m}\right) = 42000\,J$$

$$W = -42000\,J\left(\ln\frac{0.06\; m^3}{0.03\; m^3}\right) = -29112\;\; J$$

(d) work done by the gas (irreversible)

$$W = -P\int_{V_1}^{V_2} dV = -P_2(V_2 - V_1)$$

Solving for P$_2$,

$$k = P_2V_2$$

$$P_2 = \frac{k}{V_2} = \left(\frac{42000\,J}{0.06\; m^3}\right)\left(\frac{1\; N\; m}{1\,J}\right)\left(\frac{1\; Pa}{1{}^{N}\!/_{m^2}}\right) = 700000\; Pa$$

$$W = (-\;700000\; Pa)(0.06m^3 - 0.03m^3)\left(\frac{1\;{}^{N}\!/_{m^2}}{1\; Pa}\right)\left(\frac{1\,J}{1\; N\; m}\right) = -21000\,J$$

(a) process efficiency

$$\%\; efficiency = \frac{irreversible\; work}{reversible\; work}\times\; 100 = \frac{-21000\,J}{-29112\,J}\times 100 = 72\%$$

Answers:

(a) Reversible work is 29112 Joules.
(b) Irreversible work is 21000 J
(c) Process efficiency is 72%

Enthalpy, H

The enthalpy of a system is defined as the internal energy of the system plus the product of the pressure and volume of the system.

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = H_{final} - H_{initial}$$

For a given chemical reaction,

$$reactants \rightarrow products$$

The change in the enthalpy can be calculated as

$$\boldsymbol{\Delta H = \Delta H_{products} - \Delta H_{reactants}}$$

Sample Problem 10:

Calculate ΔE and ΔH for 1 kg of water when it vaporize at the constant temperature of 100°C and the constant pressure of 101.33 kPa. The specific volumes of liquid and water vapor at these conditions are 0.00104 and 1.673 m^3/kg. For this change, heat in the amount of 2256.9 kJ is added to the water. (Ans: 2087.5 kJ, 2256.9 kJ)

Given: mass = 1 kg
T = 100°C
P = 101.33 kPa
V_L = 0.00104 m^3/kg
V_g = 1.673 m^3/kg
Q = 2256.9 kJ

Required: ΔE, ΔH

Solution:

(a) Solving for ΔE

$$\Delta E = Q + W$$

$$\Delta E = Q - PdV = Q - [P\left(V_{gas} - V_{liquid}\right)]$$

$$\Delta E = 2256.9\ kJ - \left\{(101.33 kPa)\left(1.673\frac{m^3}{kg} - 0.00104\frac{m^3}{kg}\right)\left(\frac{1000\ Pa}{1\ kP}\right)\left(\frac{1\ {}^{N}/_{m^2}}{1\ Pa}\right)\left(\frac{1\ J}{1\ Nm}\right)\left(\frac{1\ kJ}{1000\ J}\right)\right\}$$

$$\Delta E = 2087.5\ \frac{kJ}{kg}$$

(a) Solving for ΔH

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + P\Delta V + V\Delta P$$

Since pressure is constant, $V\Delta P = 0$,

$$\Delta H = \Delta E + \left[P\left(V_{gas} - V_{liquid}\right)\right]$$

$$\Delta H = 2087.5\,\frac{kJ}{kg} + \left\{(101.33kPa)\left(1.673\frac{m^3}{kg} - 0.00104\frac{m^3}{kg}\right)\left(\frac{1000Pa}{1\ kPa}\right)\left(\frac{1\ {}^{N}/_{m^2}}{1\ Pa}\right)\left(\frac{1\,J}{1\ Nm}\right)\left(\frac{1\ kJ}{1000J}\right)\right\}$$

$$\Delta H = 2256.9\,\frac{kJ}{kg}$$

Answers: ΔE = 2087.5 kJ/kg; ΔH = 2256.9 kJ/kg

Activities and Assessments:

1.) When gasoline burns in an automobile engine, the heat released causes the products CO_2 and H_2O to expand, which pushes the pistons outward. Excess heat is removed by the car's cooling system. If the expanding gases do 451 J of work on the pistons and the system loses 325 J to the surroundings as heat, calculate the change in internal energy in joules.

2.) Liquid water at 180°C and 1002.7 kPa has an internal energy of 762.0 kJ/kg and a specific volume of 1.128 cm^3/g. (a) What is its enthalpy? (b) The water is brought to the vapour state at 300°C and 1500 kPa, where its internal energy is 2784.4 kJ/kg and its specific volume is 169.7 cm^3/g. Calculate the change in internal energy and the change of enthalpy for the process.

3.) Two liters of N_2 at 0°C and 5 atm pressure are expanded isothermally against a constant pressure of 1 atm until the pressure of the gas is also 1 atm. Assuming the gas to be ideal, what are the values of W, ΔE, Q and ΔH. Express you final answers in calories. (NOTE: 24.22 cal = 1 L-atm)

4.) A gas expands against a variable opposing pressure given by P = 10/V atm, where V is the volume of the gas at each stage of expansion. Further, in expanding from 10 to 100 liters, the gas undergoes a change in internal energy of ΔE = 100 cal. How much heat, in calories, is absorbed by the gas during the process? [NOTE: 1 atm = 24.22 cal]

LESSON 04: THERMOCHEMISTRY
Unit 03: Heat of Reaction

Introduction:

In the previous lesson, it was established that the internal energy and enthalpy of a system is related to both work and heat that is applied either by or to the system. In addition, the work component of the system, particularly on the concept of the PV-work, was elaborated. In this lesson, the HEAT component is put into focus particularly on combustion reactions which is the focus of the study on the relationship of fuels and energy.

Lesson Objectives:

After successful completion of this lesson, the students are expected to:

1) Differentiate constant pressure and constant volume processes.
2) Interpret thermochemical equations and enthalpy diagrams properly.
3) Solve problems involving Hess Law of Heat Summation.
4) Demonstrate an ability to solve involving enthalpies of reaction.

Course Materials:

Heats of Reaction

The **Heat of Reaction** pertains to the amount of energy that accompanies a chemical reaction. They can either be equivalent to the internal energy or the enthalpy of reactions, depending on the circumstances:

Heat of reaction at constant volume,

Consider a mechanical reversible non-flow process at constant V

$$\Delta U = Q + W$$

$$\Delta U = Q - P\int_{V_1}^{V_2} dV$$

At constant volume, dV = 0

$$\Delta U = Q$$

$$\boldsymbol{Q_v = \Delta U}$$

Heat of reaction at constant pressure,

Consider a mechanical reversible non-flow process at constant P

$$\Delta H = \Delta U + \Delta(PV)$$

From the First Law of Thermodynamics, $\Delta U = Q + W$

$$\Delta U = Q + W + \Delta(PV)$$

But W = PdV

$$\Delta U = Q - P\Delta V + P\Delta V - V\Delta P$$

At constant pressure, $\Delta P = 0$

$$\Delta U = Q$$

$$\boldsymbol{Q_P = \Delta H}$$

<u>Heat of reaction of solids and liquids at very low pressure,</u>

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + P\Delta V + V\Delta P$$

Because changes in the volumes of solids and liquids are negligible at very low pressure ($\Delta P = 0$), $\Delta V = 0$; hence,

$$\boldsymbol{\Delta H = \Delta U}$$

<u>Heat of reaction of ideal gases at constant pressure,</u>

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + P\Delta V + V\Delta P$$

At constant pressure,

$$\Delta H = \Delta U + P\Delta V$$

For an ideal gas, it obeys the ideal gas equation, PV = nRT

$$\Delta H = \Delta U + P\left(\Delta n_{ig}\frac{RT}{P}\right)$$

$$\boldsymbol{\Delta H = \Delta U + \Delta n_{ig} RT}$$

A positive value of ΔH and ΔE shows that heat is absorbed during the process while a negative value of ΔH and ΔE shows that heat is liberated during the process.

However, since most of the reactions that are considered in our study of thermochemistry are done under constant pressure, the Heat of Reaction is synonymous as the **Enthalpy of the Reaction**; hence, ∆H, instead of ∆E.

Thermochemical Equations and Enthalpy Diagrams

Thermochemical equations are balanced chemical equations that show the associated enthalpy changes.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H = -840\ kJ$$

When dealing with thermochemical equations, there are important notes that are needed to be considered:

1. Enthalpy is an extensive property.
2. The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.
3. The enthalpy change in a reaction depends on the states of the products and reactants.

Enthalpy diagrams show changes in enthalpy of a chemical reaction as the chemicals move from reactants to products and vice versa

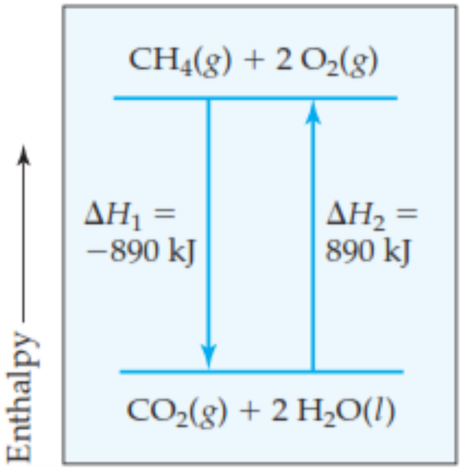


Figure 1: Enthalpy diagram of the combustion of methane. Image Source: Brown, 2011

A positive value of ∆H shows an endothermic reaction, while a negative value of ∆H shows that a reaction is exothermic.

Sample Problem 1:

Ozone, O_3(g), is a form of elemental oxygen that is important in the absorption of ultraviolet radiation in the stratosphere. It decomposes to O_2(g) at room temperature and pressure according to the following reaction:

$$2O_{3\,(g)} \rightarrow 3O_{2(g)} \qquad \Delta H = -284.6\ kJ$$

(a) What is the enthalpy change for this reaction per mole of $O_3(g)$? (b) Which has the higher enthalpy under these conditions, $2O_3(g)$ or $3O_2(g)$?

Given: Thermochemical equation for $O_3(g)$ decomposition to $O_2(g)$

Required: (a) ΔH per mole of O_3 (b) Which has higher enthalpy, $2O_3(g)$ or $3O_2(g)$

Solution:

a. Solving for the ΔH per mole of O_3

$$\Delta H = \frac{-284.6\ kJ}{2\ mol\ O_3} = -1423\ \frac{kJ}{mol\ O_3}$$

a. Solving for the molecule with higher enthalpy

$$\Delta H = \Delta H_{products} - \Delta H_{reactants}$$

$$-284.6\ kJ = \Delta H_{products} - \Delta H_{reactants}$$

$$0 > \Delta H_{products} - \Delta H_{reactants}$$

$$\Delta H_{reactants} > \Delta H_{products}$$

$$\Delta H_{2O_3} > \Delta H_{3O_2}$$

Sample Problem 2:

Consider the following reaction:

$$2Mg(s) + O_2(g) \rightarrow 2\,MgO(s) \qquad \Delta H = -1204\ kJ$$

(a) Is this reaction exothermic or endothermic?
(b) Calculate the amount of heat transferred when 3.55 g of Mg(s) reacts at constant pressure.
(c) How many grams of MgO are produced during an enthalpy change of -234 kJ?
(d) How many kilojoules of heat are absorbed when 40.3 g of MgO(s) is decomposed into Mg(s) and $O_2(g)$ at constant pressure?

Given:

a) Type of reaction
b) Q when 3.55 g of Mg is reacted

c) Grams of MgO produced for ΔH = -234 kJ
d) Q (kJ) when 40.3g of MgO is decomposed

Solution:

a) ΔH is negative; hence, the process is exothermic
b) Solving for Q when 3.55 g of Mg is reacted

$$Q = \Delta H = \left(\frac{-1204\ kJ}{2\ mol\ Mg}\right)\left(\frac{1\ mol\ Mg}{24.305\ g\ Mg}\right)(3.55\ g\ Mg) = -87.93\ kJ$$

c) Solving for Grams of MgO produced for ΔH = -234 kJ

$$mass_{MgO\ produced} = (-234\ kJ)\left(\frac{2\ mol\ MgO}{-1204\ kJ}\right)\left(\frac{40.305\ g\ MgO}{1\ mol\ MgO}\right) = 15.67\ MgO$$

d) Solving for Q (kJ) when 40.3 g of MgO is decomposed

$$Q = \Delta H = \left(\frac{1204\ kJ}{2\ mol\ MgO}\right)\left(\frac{1\ mol\ MgO}{40.305\ g\ MgO}\right)(40.3\ g\ MgO) = 602\ kJ$$

Sample Problem 3:

From the following data for three prospective fuels, calculate which could provide the most energy per unit volume:

Fuel	Density at 20°C (g/cm^3)	Molar Enthalpy of Combustion (kJ/mol)
Nitroethane, $C_2H_5NO_2$	1.052	- 1368
Ethanol, C_2H_5OH	0.789	- 1367
Methylhydrazine, CH_6N_2	0.874	- 1307

Given: Three fuels with data on density and molar enthalpy of combustion

Required: The fuel with the most energy

Solution:

a) Solving for energy from nitroethane

$$\Delta H_{nitroethane} = \frac{\left(-1368\ \frac{kJ}{mol}\right)\left(1.052\ \frac{g}{cm^3}\right)}{75\ \frac{g}{mol}} = -19.19\ kJ$$

b) Solving for energy from ethanol

$$\Delta H_{ethanol} = \frac{\left(-1367\ \frac{kJ}{mol}\right)\left(0.789\ \frac{g}{cm^3}\right)}{41\ \frac{g}{mol}} = -26.11\ kJ$$

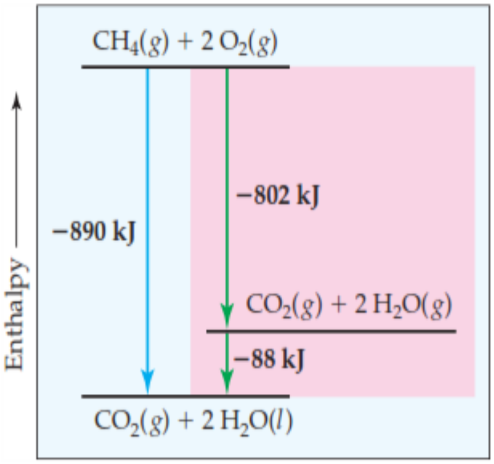
c) Solving for energy from methylhydrazine

$$\Delta H_{methylhydrazine} = \frac{\left(-1307\ \frac{kJ}{mol}\right)\left(0.874\ \frac{g}{cm^3}\right)}{42\ \frac{g}{mol}} = -27.20\ kJ$$

Answer: The fuel that can provide the most energy is methylhydrazine.

Hess' Law of Constant Summation

The heat evolved or absorbed in a given reaction must be independent of the particular manner in which the reaction takes place. Because enthalpy and internal energies are state functions, whether a particular reaction is carried out in one step or a series of steps, the sums of the enthalpy and internal changes associated with the individual steps must be the same as the enthalpy change associated with the one step process.



Hess' Law states that of a chemical reaction out in a series of steps, ΔH for the overall reaction equals the sum of the enthalpy changes for the individuals steps.

$$\begin{array}{ll} CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} & \Delta H = -802\ kJ \\ 2H_2O_{(g)} \rightarrow 2H_2O_{(l)} & \Delta H = -\ \ 88\ kJ \\ \hline CH_{4(g)} + 2O_{2(g)} + 2H_2O_{(g)} \rightarrow.\ CO_{2(g)} + 2H_2O_{(l)} + 2H_2O_{(g)} & \Delta H = -890\ kJ \end{array}$$

Net Equation:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -890\ kJ$$

Sample Problem 4:

Calculate the enthalpy change for the reaction

$$P_4O_{6(s)} + 2O_{2(g)} \rightarrow P_4O_{10(s)}$$

Given the following enthalpies of reaction:

$$P_{4(s)} + 3O_{2(g)} \rightarrow P_4O_{6(s)} \qquad \Delta H = -1640.1\ kJ. \qquad (Equation\ 01)$$

$$P_{4(s)} + 5O_{2(g)} \rightarrow P_4O_{10(s)} \qquad \Delta H = -2940.1\ kJ \qquad (Equation\ 02)$$

Given: Thermochemical reaction for the formation of P_4O_6 and P_4O_{10} from its elemental constituents

Required: Enthalpy change for

$$P_4O_{6(s)} + 2O_{2(g)} \rightarrow P_4O_{10(s)}$$

Solution:

Reverse Equation (1) then add Equation (2)

$$P_4O_{6(s)} \rightarrow P_{4(s)} + 3O_{2(g)} \qquad \Delta H = 1640.1\ kJ$$

$$P_{4(s)} + 5O_{2(g)} \rightarrow P_4O_{10(s)} \qquad \Delta H = -2940.1\ kJ$$

$$P_4O_{6(s)} + 2O_{2(g)} \rightarrow P_4O_{10(s)} \qquad \Delta H = -1300\ kJ$$

Answer: ΔH is -1300 kJ

Sample Problem 5:

From the enthalpies of reaction:

$$H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)} \qquad \Delta H = -537\ kJ \qquad (Equation\ 1)$$

$$C_{(s)} + 2F_{(2)} \rightarrow CF_{4(g)} \qquad \Delta H = -680\ kJ \qquad (Equation\ 2)$$

$$2C_{(s)} + 2H_{2(g)} \rightarrow C_2H_{4(g)} \qquad \Delta H = +52.3\ kJ \qquad (Equation\ 3)$$

Calculate ΔH for the reaction of ethylene with F_2:

$$C_2H_{4(g)} + 6F_{2(g)} \rightarrow 2CF_{4(g)} + 4HF_{(g)}$$

Given: Thermochemical reaction for the formation of HF, CF_4 and C_2H_4 from its elemental constituents

Required: Enthalpy change for

$$C_2H_{4(g)} + 6F_{2(g)} \rightarrow 2CF_{4(g)} + 4HF_{(g)}$$

Solution:

Multiply equation (1) by 2; multiply equation (2) by 2; Reverse equation 3. Add them altogether.

$$2H_{2(g)} + 2F_{2(g)} \rightarrow 4HF_{(g)} \qquad \Delta H = (-537\ kJ)(2)$$

$$2C_{(s)} + 4F_{(2)} \rightarrow 2CF_{4(g)} \qquad \Delta H = (-680\ kJ)(2)$$

$$C_2H_{4(g)} \rightarrow 2\ C_{(s)} + 2H_{(2)} \qquad \Delta H = -52.3\ kJ$$

$$C_2H_{4(g)} + 6F_{2(g)} \rightarrow 2CF_{4(g)} + 4HF_{(g)} \qquad \Delta H = -2486.3\ kJ$$

Answer: ΔH is -2486.3 kJ

Common Enthalpies of Reaction

Enthalpy of Formation (Heat of Formation, ΔH_f) refers to the thermal change involved in the formation of a substance from its constituent elements

$$A + B + C \rightarrow ABC \qquad \Delta H_f =$$

Enthalpy of Vaporization (Latent Heat of Vaporization, ΔH_{vap}) refers to the amount of heat used in converting liquids to gases; also called “latent heat of vaporization”

$$A_{liquid} \rightarrow A_{vapor} \qquad \Delta H_{vap} =$$

Enthalpy of Fusion (Latent Heat of Fusion, ΔH_{fus}) refers to the amount of heat used for melting solids; also called “latent heat of fusion”

$$A_{solid} \rightarrow A_{liquid} \qquad \Delta H_{fus} =$$

Enthalpy of Combustion (Heat of Combustion) refers to the amount of heat liberated per mole of a substance burned

$$Fuel + O_2 \rightarrow CO_2 + H_2O \qquad \Delta H_c =$$

Standard Enthalpies of Reaction, ΔH°

It should be noted that the magnitude of any enthalpy change depends on the temperature, pressure and state of the reactants and products. With this, it is important to establish a standard basis when dealing with enthalpies of reaction to keep the scope within a narrow range.

More often than not, the standard state of a substance is considered as a standard basis; hence, the enthalpy accompanying a reaction involving substances in their standard states is known as the **Standard Enthalpy of a Reaction, ΔH°.**

The standard state of a substance is its pure form at atmospheric pressure (1 atm) and the temperature of interest which is usually chosen to be 298K (25°C).

The standard enthalpy of a reaction is calculated as,

$$\boldsymbol{\Delta H^{\circ}{}_{reaction} = \sum n\,\Delta H^{\circ}_{f_{products}} - \sum n\,\Delta H^{\circ}_{f_{reactants}}}$$

Standard Enthalpies of Formation of a compound, $\Delta H_f°$

The **Standard Enthalpy of Formation** of a compound is the change in enthalpy for the reaction that forms from one mole of the compound from its elements with all substances in their standard states.

$$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad \Delta H^{\circ}_f = -17890\,cal$$

The Standard Enthalpies of Formation can be accessed through the appendices of this module.

Sample Problem 6:

Ethanol (C_2H_5OH) is currently blended with gasoline as an automobile fuel. (a) Write a balanced equation for the combustion of liquid ethanol in air. (b) Calculate the standard enthalpy change for the reaction, assuming H_2O(g) as product. (c) Calculate the heat produced per liter of ethanol by combustion of ethanol under constant pressure. Ethanol has a density of 0.789 g/mL. (d) Calculate the mass of CO_2 produced per kJ f heat emitted.

Given: Liquid ethanol with density of 0.789 g/mL burning in air

Required:

a) Balanced equation for the combustion of liquid ethanol in air.
b) Standard enthalpy change for the reaction, assuming H_2O(g) as product.
c) Heat produced per liter of ethanol
d) Calculate the mass of CO_2 produced per kJ f heat emitted.

Solution:

a) Balanced combustion equation

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

b) Standard enthalpy change for the reaction

$$\Delta H°_{rxn} = \sum n\Delta H°_{products} - \sum n\Delta H°_{reactants}$$

$$\Delta H°_{rxn} = \left[\left(n_{CO_{2(g)}}\right)\left(\Delta H^{\circ}_{f\,CO_{2(g)}}\right) + \left(n_{H_2O_{(g)}}\right)\left(\Delta H^{\circ}_{f\,H_2O_{(g)}}\right)\right] - \left[\left(n_{C_2H_5OH_{(l)}}\right)\left(\Delta H^{\circ}_{f\,C_2H_5OH_{(l)}}\right) + \left(n_{O_{2(g)}}\right)\left(\Delta H^{\circ}_{f\,CO_{2(g)}}\right)\right]$$

$$\Delta H°_{rxn} = \left[(2mol)\left(-393.5\,\frac{kJ}{mol}\right) + (3mol)\left(-241.82\,\frac{kJ}{mol}\right) - \left[(1mol)\left(-277.7\frac{kJ}{mol}\right) + (3mol)\left(0\,\frac{kJ}{mol}\right)\right]\right]$$

$$\Delta H°_{rxn} = -1234.76\,kJ$$

c) Heat produced per liter of ethanol

$$Q = \Delta H = \left(1234\,\frac{kJ}{mol\;C_2H_5OH}\right)\left(\frac{1\;mol\;C_2H_5OH}{46\;g\;C_2H_5OH}\right)\left(0.789\,\frac{g}{mL}\right)\left(\frac{1000\;mL}{1\;L}\right)$$

$$Q = 21179\,\frac{kJ}{L}$$

d) Mass of CO_2 produced

$$Mass\;of\;CO_2\;produced = \left(\frac{2\;mol\;CO_2}{1234.76\;kJ}\right)\left(\frac{44\;g}{1\;mol\;CO_2}\right) = 0.0712\;g\;CO_2$$

Activities and Assessments:

1.) It is interesting to compare the “fuel value” of a hydrocarbon in a world where fluorine rather than oxygen is the combustion agent. The enthalpy of formation of $CF_4(g)$ is -679.9 kJ/mol. The enthalpy of formation two reactions is the more exothermic?

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

$$CH_4(g) + 4\,F_2(g) \longrightarrow CF_4(g) + 4\,HF(g)$$

2.) Calculate the standard enthalpy of formation of gaseous di-borane (B_2H_6) using the following thermochemical information:

$$
\begin{array}{ll}
4\,\mathrm{B}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{B_2O_3}(s) & \Delta H^\circ = -2509.1\ \mathrm{kJ} \\
2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(l) & \Delta H^\circ = -571.7\ \mathrm{kJ} \\
\mathrm{B_2H_6}(g) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{B_2O_3}(s) + 3\,\mathrm{H_2O}(l) & \Delta H^\circ = -2147.5\ \mathrm{kJ}
\end{array}
$$

3.) At the end of 2009, global population was about 6.8 billion people. What mass of glucose ($C_6H_{12}O_6$) in kg would be needed to provide 1500 Cal/person/day of nourishment to the global population for one year? Assume that glucose is metabolized entirely to CO_2 and $H_2O(l)$.

LESSON 04: THERMOCHEMISTRY
Unit 04: Calorimetry

Introduction:

Thermal changes that accompany a chemical reaction can be determined using calorimeters which operates under the First Law of Thermodynamics. This lesson presents the basic concepts of calorimetry.

Lesson Objectives:

After successful completion of this lesson, the students are expected to:

1) Define heat capacity and discuss its importance.
2) Solve problems related to heat capacity of a system.
3) Demonstrate the understanding of the First Law of Thermodynamics as applied in calorimetry.
4) Solve problems involving calorimetry.

Course Materials:

Calorimetry

The amount of heat resulting from chemical reactions can be determined experimentally through the system of **calorimetry**. Calorimetry uses the principle of the First Law of Thermodynamics: the amount of heat that was lost from an object or a substance is the same amount as the heat gained by another.

Heat Capacity

An object has the capacity to maintain its temperature until a corresponding amount of heat is introduced to it is capable to increase its temperature. The amount of heat required for the object to raise its temperature by one Kelvin is known as the object's **heat capacity**.

The heat capacity of one gram of a substance is known as its **specific heat capacity** and is also known as the **specific heat** of the object or substance. When the reference is one mole o the substance, it is called the **molar heat capacity**.

The heat capacity of a substance can be determined experimentally by measuring the temperature change that a known mass of the substance undergoes when it gains or loses specific quantity of heat.

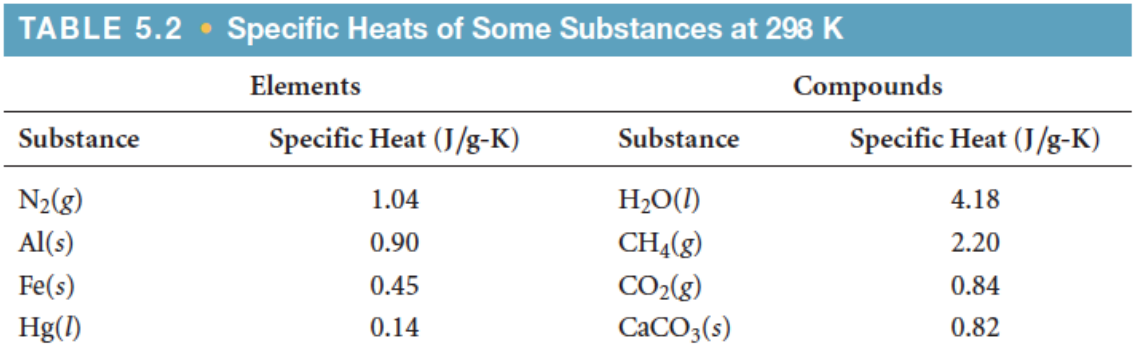


TABLE 5.2 • Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	Specific Heat (J/g-K)	Substance	Specific Heat (J/g-K)
$N_2(g)$	1.04	$H_2O(l)$	4.18
$Al(s)$	0.90	$CH_4(g)$	2.20
$Fe(s)$	0.45	$CO_2(g)$	0.84
$Hg(l)$	0.14	$CaCO_3(s)$	0.82

Specific Heat (C_p) Calculations

Base on the definition of specific heat,

$$Specific\ Heat, C_p = \frac{Quantity\ of\ heat\ transferred, Q}{(grams\ of\ the\ substance, m)(Temperature\ change, \Delta T)}$$

$$C_p = \frac{Q}{m\ \Delta T}$$

$$Q = mC_p\Delta T$$

Calorimeter

A calorimeter is a device used to measure thermal changes. It has two main classification:

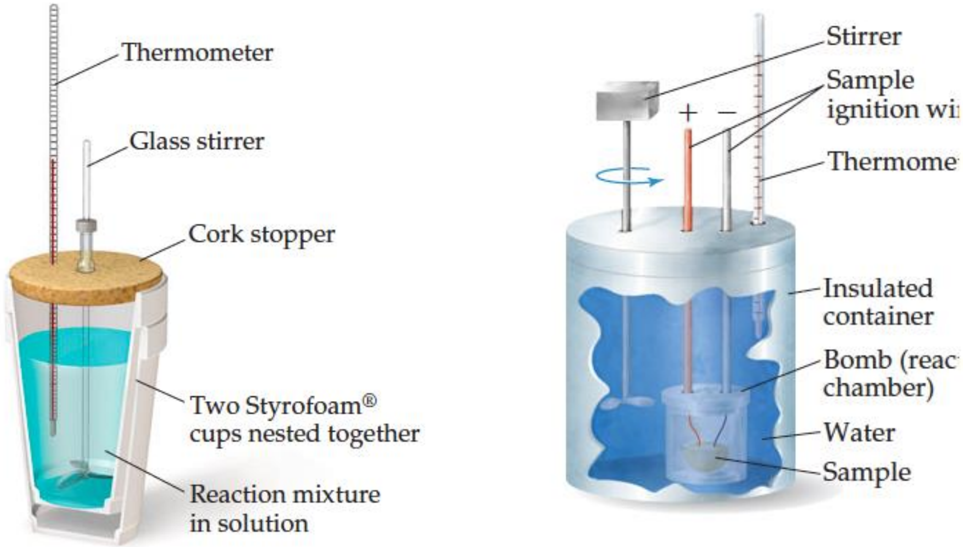


Figure 1: Constant-pressure and constant-volume calorimeters.

1) **The Constant-Pressure Calorimeter**

The working principle behind the constant pressure calorimeter is that the heat of reaction in the solution is absorbed by the solution. This calorimeter is being used to measure the heat transferred in processes open to atmosphere and is used to find the specific heat capacity of a solid that does not react with or dissolved in water.

$$-Q_{lost} = Q_{gained}$$

$$-Q_{lost\ by\ the\ reaction} = Q_{gained\ by\ the\ solution}$$

$$-Q_{lost\ by\ the\ reaction} = (mass_{solution})(heat\ capacity_{solutin})(\Delta T_{solution})$$

$$-Q_{rxn} = (m\ Cp\ \Delta T)_{solution}$$

2) Constant-Volume Calorimetry (Bomb calorimetry)

The working principle behind the constant volume calorimeter is that the heat of combustion coming from the reaction of fuel and oxygen inside the device is absorbed by the calorimeter. This calorimeter is being used to measure precisely the heat released in a combustion reaction.

$$-Q_{lost} = Q_{gained}$$

$$-Q_{lost\ by\ the\ reaction} = Q_{gained\ by\ the\ calorimeter}$$

$$-Q_{lost\ by\ the\ reaction} = (Specific\ heat_{calorimeter})(\Delta Temperature_{calorimeter})$$

$$-Q_{rxn} = C_{cal}\ \Delta T$$

Sample Problem 1:

The molar heat of combustion of naphthalene (MW =128.17 g/mol) is -1228.2 kcal/mole. If 0.300g of naphthalene burned in a calorimeter causes a rise in temperature of 2.050°C, what is total heat capacity of the calorimeter?

Given: ΔHc = -1228.2 kcal/mole
MW = 128. 17 g/mol
M = 0.300 g
ΔT = 2.050°C

Required: C_{cal}

Solution:

$$-Q_{lost} = Q_{gained}$$

$$-Q_{lost\ by\ the\ reaction} = Q_{gained\ by\ the\ calorimeter}$$

$$-Q_{rxn} = C_{cal}\,\Delta T$$

$$-\Delta H_c = C_{cal}\,\Delta T$$

$$C_{cal} = \frac{-\Delta H_c}{\Delta T} = \frac{-\left(-1228.2\,\frac{kcal}{mol}\right)\left(\frac{1\,mol}{128.17\,g}\right)(0.300\,g)\left(\frac{1000\,cal}{1\,kcal}\right)}{2.050\,℃} = 1402\,\frac{cal}{℃}$$

Sample Problem 2:

Two iron bolts of equal mass – one at 100°C, the other at 55°C – are placed in an insulated container. Assuming that the heat capacity of the calorimeter is negligible, what is the final temperature inside the container. Specific heat of iron is 0.450 J/g-K.

Given: Two iron bolts
$m_{hot} = m_{cold}$
$T_{hot,\ initial} = 100°C$
$T_{cold,\ initial} = 55°C$
$Cp_{,cal} = 0$ J/K
$Cp_{metal} = 0.450$ J/g-K

Required: T_{final}

Solution:

$$-Q_{lost} = Q_{gained}$$

$$-Q_{lost\ by\ the\ heat\ metal} = Q_{gained\ by\ cold\ metal}$$

$$-\left(m\,C_p\,\Delta T\right)_{hot\ metal} = \left(m\,C_p\,\Delta T\right)_{cold\ metal}$$

$$\left(-\,C_p\left(T_{final} - T_{initial}\right)\right)_{hot\ metal} = \left(C_p\left(T_{final} - T_{initial}\right)\right)_{cold\ metal}$$

$$-C_p\left(T_{final} - 100℃\right) = Cp\left(T_{final} - 55℃\right)$$

$$\left(-C_p\,T_{final}\right) + 100℃\,C_p = \left(C_p\,T_{final}\right) - 55℃\,C_p$$

$$-2\,C_p\,T_{final} = (-55℃ - 100℃)\,C_p$$

$$T_{final} = \frac{-155\,℃}{-2} = 77.5\,℃$$

Answer: Final temperature is 77.5°C

Sample Problem 3:

Under constant-volume conditions, the heat of combustion of glucose ($C_6H_{12}O_6$) is 15.57 kJ/g. A 3.500-g sample of glucose is burned in a bomb calorimeter The temperature of the calorimeter is increased form 20.94°C to 24.72°C. (a) What is the total heat capacity of the calorimeter? (b) If the size of the glucose sample has been exactly twice as large, what would the temperature change of the calorimeter have been?

Given: constant-volume calorimetry
$\Delta Hc = - 15.57$ kJ/g
m = 3.500 g
$C_6H_{12}O_6$
$T_{initial} = 20.94$ °C
$T_{final} = 24.72$°C

Required: (a) Ccal; (b) If $m_2 = 2m_1$, what is ΔT

Solution:

$$-Q_{lost} = Q_{gained}$$

$$-Q_{lost\ by\ the\ reaction} = Q_{gained\ by\ the\ calorimeter}$$

$$-Q_{rxn} = C_{cal}\,\Delta T$$

$$-\Delta H_c = C_{cal}\,\Delta T$$

$$C_{cal} = \frac{-\Delta H_c}{\Delta T} = \frac{-\left(-15.57\ \frac{kJ}{g}\right)(3.500\ g)}{24.72℃ - 20.94℃} = 14.42\ \frac{kJ}{℃}$$

Answer: The specific heat of the calorimeter is 14.42 kJ/°C.

Solution:

$$-Q_{lost} = Q_{gained}$$

$$-Q_{lost\ by\ the\ reaction} = Q_{gained\ by\ the\ calorimeter}$$

$$-Q_{rxn} = C_{cal}\,\Delta T$$

$$-\Delta H_c = C_{cal}\,\Delta T$$

$$\Delta T = \frac{-\Delta H_c}{C_{cal}} = \frac{-\left(-15.57\ \frac{kJ}{g}\right)(3.500\ g)(2)}{14.42\ \frac{kJ}{°\mathrm{C}}} = 7.56°\mathrm{C}$$

Answer: The change in temperature is 7.56°C.

Sample Problem 4:

You place 50.0 mL of 0.500M NaOH in a coffee-cup calorimeter at 25.00°C and carefully add 25.00mL of 0.500M HCl, also at 25.00°C. After stirring the final temperature is 27.21°C. Calculate the heat of the solution in J and the change in enthalpy in kJ per mol of water produced. Assume the total volume is the sum of the individual volumes and that the final solution has the same density and specific heat as water: ρ = 1.00 g/mL and Cp = 4.184 J/g-K.

Given: V_{NaOH} = 50.0mL
M_{NaOH} = 0.500 M
T_{NaOH} = 25.00°C
V_{HCl} = 25.00 mL
M_{HCl} = 0.500 M
T_{HCl} = 25.00°C
T_{final} = 27.21°C
ρ_{soln} = 1.00 g/mL
$C_{p,soln}$ = 4.184 J/g-K

Required: (a) $Q_{solution}$, J (b) ΔH, kJ /mol

Solution:

(a) Solving for the heat of solution

$$NaOH + HCl \rightarrow H_2O + NaCl$$

$$Q_{solution} = \left(m\ C_p\ \Delta T\right)_{solution}$$

$$Q_{solution} = \left(\rho\ V\ C_p\ \left(T_{final} - T_{initial}\right)\right)_{solution}$$

$$Q_{solution} = \left(1.00\ \frac{g}{mL}\right)(50.00\ mL + 25.00\ mL)\left(4.184\ \frac{J}{g-K}\right)(27.21°\mathrm{C} - 25.00°\mathrm{C}) = 693\ J$$

(b) Solving for the change in enthalpy per mole of water produced

$$-Q_{lost\ by\ the\ reaction} = Q_{gained\ by\ the\ solution}$$

$$Q_{lost\ by\ the\ reaction} = -Q_{gained\ by\ the\ solution}$$

$$Q_{lost\ by\ the\ reaction} = -693\ J$$

Assume NaOH as the limiting reactant,

$$mole_{H_2O} = \left(0.500\ \frac{mol\ NaOH}{L}\right)(50\ mL)\left(\frac{1\ L}{1000\ mL}\right)\left(\frac{1\ mol\ H_2O}{1\ mol\ NaOH}\right) = 0.025\ mol$$

Assume HCl as the limiting reactant

$$mole_{H_2O} = \left(0.500\ \frac{mol\ HCl}{L}\right)(25\ mL)\left(\frac{1\ L}{1000\ mL}\right)\left(\frac{1\ mol\ H_2O}{1\ mol\ HCl}\right) = 0.0125\ mol$$

HCl is the limiting reactant; hence there are 0.0125 moles of water produced.

$$\Delta H = \frac{Q_{reaction}}{mole\ H_2O\ produced} = \frac{-693\ J}{0.0125\ mol}\left(\frac{1\ kJ}{1000\ J}\right) = -55\ \frac{kJ}{mol}$$

Answers: The heat of solution is 693 J and the change in enthalpy is – 55 kJ per mole of water produced.

Activities and Assessment:

1.) When a 0.235-g sample of benzoic acid is combustion in a bomb calorimeter, the temperature rises 1.642°C. When a 0.265-g sample of caffeine, $C_8H_{10}O_2N_4$, is burned, the temperature rises 1.525°C. Using the value 26.38 kJ/g for the heat of combustion of benzoic acid, calculate the heat of combustion per mole of caffeine at constant volume.

2.) If 25 J are required to change the temperature of 5.0 g of substance A by 2.0°C, what is the specific heat of substance A?

3.) Derive the formula for the calculation of the Calorimeter constant, $Cp,_{calorimeter}$ used in Experiment No. 2 entitled Calorimetry.

$$C_{p,calorimeter} = C_{p,water}\left[\frac{(m_{hot\ water})(T_H - T_F) - (m_{cold\ water})(T_F - T_c)}{T_F - T_C}\right]$$

Where
m = mass
T_F = final temperature
T_H = higher temperature
T_C = colder temperature

LESSON 05: SOLUTIONS THERMODYNAMICS

Unit 01: Spontaneity

Introduction:

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment.

- A **spontaneous process** is one that occurs naturally under certain conditions.
- A **nonspontaneous process**, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source.

A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction.
At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Distinguish between spontaneous and nonspontaneous processes
2. Describe the dispersal of matter and energy that accompanies certain spontaneous processes

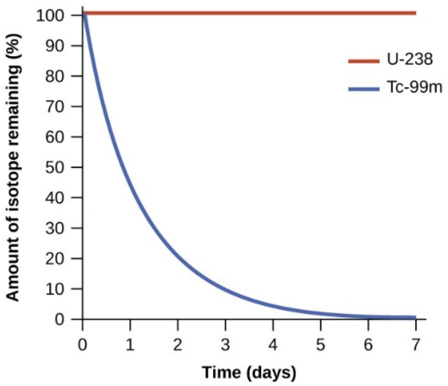
Course Materials:

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time.

To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely.

Spontaneity comparison:

Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years.



Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

Dispersal of Matter and Energy

Consider an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty ($P = 0$). When the valve is opened, the gas spontaneously expands to fill both flasks equally. According from the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

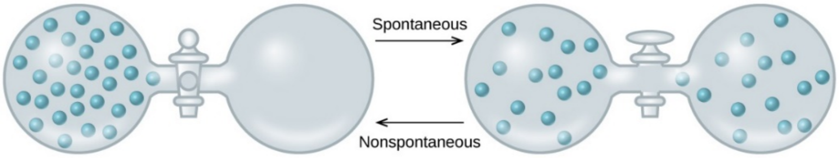
$$\mathbf{W = -P\Delta V = 0 \qquad (P = 0 \text{ in a vacuum})}$$

Note: That since the system is isolated, no heat has been exchanged with the surroundings ($q = 0$). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

$$\mathbf{\Delta U = q + w = 0 + 0 = 0}$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand.

In this illustration, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).



An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Two objects at different temperatures:

When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

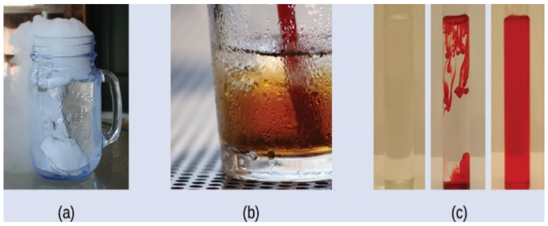
From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.

$T_X > T_Y$ X and Y in contact

Note: When two objects at different temperatures come in contact, *heat spontaneously flows from the hotter to the colder object.*

Example: Describe how matter is redistributed when the following spontaneous processes take place:
(a) A solid sublimes.
(b) A gas condenses.
(c) A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution:



(a) **Sublimation** is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.

(b) **Condensation** is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.

(c) **Diffusion**, this process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Activities and Assessment:

1. What is a spontaneous reaction?
2. What is a nonspontaneous reaction?
3. Indicate whether the following processes are spontaneous or nonspontaneous.
   a. Liquid water freezing at a temperature below its freezing point
   b. Liquid water freezing at a temperature above its freezing point
   c. The combustion of gasoline
   d. A ball thrown into the air
   e. A raindrop falling to the ground
   f. Iron rusting in a moist atmosphere

4. A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

5. Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

LESSON 05: SOLUTIONS THERMODYNAMICS
Unit 02: Entropy

Introduction:

Entropy (*S*), the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Because work is obtained from ordered molecular motion, the amount of **entropy** is also a measure of the molecular disorder, or randomness, of a system.

Two equivalent definitions of **entropy**: *the thermodynamic definition and the statistical mechanics definition.* Historically, the classical thermodynamics definition developed first.

- **The Classical Thermodynamics**, the microscopic details of a system are not considered. Instead, the behavior of a system is described in terms of a set of empirically defined thermodynamic variables, such as temperature, pressure, entropy, and heat capacity.

- **The Statistical Definition of Entropy**, defined in terms of the statistics of the motions of the microscopic constituents of a system e.g. Newtonian particles constituting a gas, and later quantum-mechanically (photons, phonons, spins, etc.).

There are many thermodynamic properties that are functions of state. This means that at a particular thermodynamic state (which should not be confused with the microscopic state of a system), these properties have a certain value. For instance, a quantity of gas at a particular temperature and pressure has its state fixed by those values and thus has a specific volume that is determined by those values.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Define entropy.
2. Explain the relationship between entropy and the number of microstates
3. Predict the sign of the entropy change for chemical and physical processes

Course Materials:

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot. published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot's findings by Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place.

In 1865, Clausius named the concept of ***S***, "the differential of a quantity which depends on the configuration of the system," ***entropy*** **(*Entropie*)** after the Greek word for 'transformation'.

$$\Delta S = \frac{Q_{rec}}{T}$$

This new property was expressed as the ratio of the ***reversible*** **heat (**q_{rev}**)** and the **kelvin temperature (*T*).** In thermodynamics, a **reversible process** is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change in some condition.

Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the *number of* ***microstates*** **(*W*)** possible for the system. A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$\mathbf{S = k\ln W}$$

Where: *k* is the Boltzmann constant, 1.38 ×× 10^{-23} J/K.

- As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\mathbf{\Delta S = S_f - S_i = k\ln W_f - k\ln W_i = k\ln W_f\ W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs

Predicting the Sign of Δ*S*

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes.

Examples:

1**.** Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

(a) One mole liquid water at room temperature ⟶ one mole liquid water at 50 °C

(b) $Ag^{+(}{}_{aq)} + Cl^{-}{}_{(aq)} \longrightarrow AgCl_{(s)}$

(c) $C_6H_{6(l)} + 15O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$

(d) $NH_{3(s)} \longrightarrow NH_{3(l)}$

Answers:

(a) positive, temperature increases
(b) negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter

(c) negative, net decrease in the amount of gaseous species
(d) positive, phase transition from solid to liquid, net increase in dispersal of matter

2. Predict the sign of the entropy change for the following processes. Give a reason for your prediction.
(a) $NaNO_{3(s)} \longrightarrow Na^{+}_{(aq)} + NO^{3-(}{}_{aq)}$

(b) the freezing of liquid water

(c) $CO_{2(s)} \longrightarrow CO_{2(g)}$

(d) $CaCO_{(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$

Answers:
(a) Positive; The solid dissolves to give an increase of mobile ions in solution.
(b) Negative; The liquid becomes a more ordered solid.
(c) Positive; The relatively ordered solid becomes a gas.
(d) Positive; There is a net increase in the amount of gaseous species.

Activities and Assessment:

1. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.
(a) $C_2H_5OH_{(l)}$ or $C_3H_7OH_{(l)}$

(b) $C_2H_5OH_{(l)}$ or $C_2H_5OH_{(g)}$

(c) $2H_{(g)}$ or $H_{(g)}$

2. Write the balanced chemical equation for the combustion of benzene, $C_6H_{6(l)}$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

3. Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $Pb^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow PbS_{(s)}$

(b) $2Fe_{(s)} + O_{2(g)} \longrightarrow Fe_2O_{2(s)}$

(c) $2C_6H_{14(l)} + 19O_{2(g)} \longrightarrow 14H_2O_{(g)} + 12CO_{2(g)}$

LESSON 05: SOLUTIONS THERMODYNAMICS
Unit 03: The Second and the Third Laws of Thermodynamics

Introduction:

The First Law of Thermodynamics provides the definition of the internal energy of a thermodynamic system, and expresses " The Law of Conservation of Energy."

The Second Law of Thermodynamics states that, "the heat energy cannot transfer from a body at a lower temperature to a body at a higher temperature without the addition of energy."

For example, when a path for conduction and radiation is made available, heat always flows spontaneously from a hotter to a colder body. Such phenomena are accounted for in terms of *entropy*. This is why running an air conditioner for a long period of time, costs you money.

The Third Law of Thermodynamics states that, regarding the properties of closed systems in thermodynamic equilibrium: "The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches absolute zero (0 K)."

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. State and explain the second and third laws of thermodynamics
2. Calculate entropy changes for phase transitions and chemical reactions under standard conditions

Course Materials:

A. The Second Law of Thermodynamics

The System and The Surroundings

Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; considering entropy changes to include *the surroundings*. In thermodynamics, the system and surroundings comprise everything, that is, the universe:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

The process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.*

Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{sys} = \frac{-Qrev}{T_{sys}} \quad and \quad \Delta S_{surr} = \frac{Q_{rev}}{T_{surr}}$$

The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

$$\mathbf{|\Delta Ssys| < |\Delta Ssurr| \qquad \Delta Suniv = \Delta Ssys + \Delta Ssurr > 0}$$

The objects are at different temperatures, and heat flows from the cooler to the hotter object. Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{sys} = \frac{Qrev}{T_{sys}} \quad and \quad \Delta S_{surr} = \frac{-Q_{rev}}{T_{surr}}$$

The signs of $\boldsymbol{q_{\text{rev}}}$ denote the gain of heat by the system and the loss of heat by the surroundings. In this case, the signs of the heat changes (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*

2. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, *the entropy change of the universe is zero, and the system is at equilibrium.*

$$\mathbf{|\Delta Ssys| \approx |\Delta Ssurr| \qquad \Delta Suniv = \Delta Ssys + \Delta Ssurr = 0}$$

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the **Second Law of Thermodynamics**: *all spontaneous changes cause an increase in the entropy of the universe.*

The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	at equilibrium

Example:

1. Will Ice Spontaneously Melt?

The entropy change for the process

$$H_2O_{(s)} \longrightarrow H_2O_{(l)}$$

….is 22.1 $\frac{J}{K}$ and requires that the surroundings transfer 6.00 kJ of heat to the system. a) Is the process spontaneous at −10.00 °C? b) Is it spontaneous at +10.00 °C?

Solution:

We can assess the spontaneity of the process by calculating the entropy change of the universe.

- If ΔS_{univ} is positive, then the process is spontaneous.

At both temperatures, $\Delta S_{\text{sys}} = 22.1 \frac{J}{K}$ and $q_{\text{surr}} = -6.00$ kJ.

a) At −10.00 °C (263.15 K), the following is true:

$$\mathbf{\Delta Suniv = \Delta Ssys + \Delta Ssurr}$$

$$= \Delta Ssys + \frac{q_{surr}}{T} = 22.1 \frac{J}{K} + \frac{-6.00\ x\ 10^3 J}{263.15\ K} = -\ 0.7 \frac{J}{K}$$

$S_{\text{univ}} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

b) At 10.00 °C (283.15 K), the following is true:

$$\mathbf{\Delta Suniv = \Delta Ssys +} \frac{q_{surr}}{T}$$

$$T = 22.1 \frac{J}{K} + \frac{-6.00\ x\ 10^3 J}{263.15\ K} = +0.9 \frac{J}{K}$$

$S_{\text{univ}} > 0$, so melting *is* spontaneous at 10.00 °C.

B. The Third Law of Thermodynamics

This system may be described by a single microstate, as its purity, perfect crystal and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal **(*W* = 1).**

According to the Boltzmann equation, the entropy of this system is zero.

$$\mathbf{S = k\ln W = k\ln (1) = 0}$$

- This limiting condition for a system's entropy represents **The Third Law Of Thermodynamics**: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Standard Entropies (*S*°)

The **standard molar entropy, S°,** is the entropy of 1 mole of a substance in its standard state, at 1 atm of pressure and a temperature of 298.15 K.

- Units in joules per mole kelvin ($\frac{J}{mol-K}$). Unlike *standard* enthalpies of formation, the value of S° is absolute.

2. The Standard Entropy Change (Δ*S*°)

Changes in entropy are associated with phase transitions and chemical reactions. Chemical equations make use of the standard molar entropy of reactants and products to find the standard entropy of reaction:

$$\Delta S^\circ_{(reaction)} = \sum nS^\circ_{(products)} - \sum nS^\circ_{(reactants)}$$

Where: **n (no. of mole)** represents stoichiometric coefficients in the balanced equation representing the process.

For example**, Δ*S*°** for the following reaction at room temperature

$$mA + nB \longrightarrow xC + yD$$

is computed as:

$$\Delta S^\circ_{(reaction)} = [\ xS^\circ(C) + yS^\circ(D)\ ] - [\ mS^\circ(A) + nS^\circ(B)\ ]$$

Example:

1. Calculate the standard entropy change for the following process:

$$H_2O_{(g)} \longrightarrow H_2O_{(l)}$$

Solution:

Calculate the entropy change using standard entropies using the **S° value from the Table:**

$$\Delta S^\circ = (1mol)\ (70.0\ \frac{J}{mol.K}) - (1mol)\ (188.8\ \frac{J}{mol.K}) = -118.8\ \frac{J}{K}$$

- The value for Δ*S*° is negative, as expected for this phase transition (condensation).

2. Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$$2CH_3OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 4H_2O_{(l)}$$

Solution:

Calculate the entropy change using standard entropies **S° value from the Table:**

$$\Delta S^\circ = \sum nS^\circ_{(products)} - \sum nS^\circ_{(reactants)}$$

Solving for ΔS°

$$\Delta S^\circ = [\ 2mol \times S^\circ(CO_{2(g)}) + 4mol \times S^\circ(H_2O_{(l)})\ ] - [\ 2mol \times S^\circ(CH_3OH_{(l)}) + 3mol \times S^\circ(O_{2(g)})\ ]$$
$$= \{ [2\ mol\ (213.8\ \frac{J}{mol.K}) + 4\ mol\ (70.0 \frac{J}{mol.K})\ ] - [\ 2mol\ (126.8 \frac{J}{mol.K}) + 3mol\ (205.03 \frac{J}{mol.K})\ ] \}$$
$$= -161.1\ \frac{J}{K}$$

Activities and Assessment:

1. Calculate the standard entropy change for the following process:

$$H_{2(g)} + C_2H_{4(g)} \longrightarrow C_2H_{6(g)}$$

2. Calculate the standard entropy change for the following reaction:

$$Ca(OH)_{2(s)} \longrightarrow CaO_{(s)} + H_2O_{(l)}$$

3. By calculating **Δ*S*univ** at each temperature, determine if the melting of 1 mole of $NaCl_{(s)}$ is spontaneous at 500 °C and at 700 °C.

   S° $NaCl_{(s)}$ = $72.11 \frac{J}{mol.K}$ S° $NaCl_{(l)}$ = $95.06 \frac{J}{mol.K}$ $\Delta H°_{fusion} = 27.95 \frac{kJ}{mol}$

- What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

4. Determine the entropy change for the combustion of gaseous propane, C_3H_8, under the standard conditions to give gaseous carbon dioxide and water.

5. Calculate ΔS° for the following changes, **ΔS° value from the Table:**

   (a) $SnCl_{4(l)} \longrightarrow SnCl_{4(g)}$

   (b) $CS_{2(g)} \longrightarrow CS_{2(l)}$

   (c) $Cu_{(s)} \longrightarrow Cu_{(g)}$

   (d) $H_2O_{(l)} \longrightarrow H_2O_{(g)}$

   (e) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$

   (f) $2HCl_{(g)} + Pb_{(s)} \longrightarrow PbCl_{2(s)} + H_{2(g)}$

   (g) $Zn_{(s)} + CuSO_{4(s)} \longrightarrow Cu_{(s)} + ZnSO_{4(s)}$

LESSON 05: SOLUTIONS THERMODYNAMICS
Unit 04: Gibb’s Free Energy

Introduction:

Gibb’s Free Energy (G) defined as the amount of "free" or "useful" energy available to do work. The Gibbs free energy, originally called *available energy*, was developed in the 1870s by the American scientist **Josiah Willard Gibbs**. In 1873, Gibbs described this "available energy" as:
“The greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition.”
According to the second law of thermodynamics, for systems reacting at standard conditions for temperature and pressure (or any other fixed temperature and pressure), there is a general natural tendency to achieve a minimum of the Gibbs free energy.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Define Gibbs free energy, and describe its relation to spontaneity
2. Calculate free energy change for a process using free energies of formation for its reactants and products
3. Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products
4. Explain how temperature affects the spontaneity of some processes
5. Relate standard free energy changes to equilibrium constants

Course Materials

Gibbs Free Energy (*G*) (or simply the *free energy*), is the amount of "free" or "useful" energy available to do work. is defined in terms of a system’s enthalpy and entropy as the following:

$$\mathbf{G = H - TS}$$

where:

T is the temperature (SI unit: kelvin),
S is the entropy (SI unit: joule per kelvin),
H is the enthalpy (SI unit: joule).

An alternative approach involving new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs.

A. Free Energy Change (Δ*G*) may be expressed as the following: Free energy is a state function, and at constant temperature and pressure,

$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

Where: ***ΔH*** is the difference between the energy (Enthalpy) produced by the process
TΔS is the energy lost to the surroundings

ΔG is the difference between the energy produced and the energy lost is the energy available (or “free”) to do useful work by the process

The first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, so this expression may be rewritten as:

$$\mathbf{\Delta S_{univ} = \Delta S - \Delta H T}$$

Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{univ} = 0$	$\Delta G = 0$	at equilibrium

B. Using Standard Enthalpy and Entropy Changes to Calculate ΔG°

One method involves the use of standard enthalpies and entropies to compute **Standard Free Energy Changes, ΔG°**, according to the following relation.

$$\mathbf{\Delta G° = \Delta H° - T\Delta S°}$$

Example:

1. Use standard enthalpy and entropy data to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

Solution:

The process of interest is the following:

$H_2O_{(l)} \longrightarrow H_2O_{(g)}$

The standard change in free energy may be calculated using the following equation:

$\Delta G° = \Delta H° - T\Delta S°$

Substance	ΔH° $(\frac{kJ}{mol})$	S° $(\frac{J}{mol.K})$
$H_2O_{(l)}$	−286.83	70.0
$H_2O_{(g)}$	−241.82	188.8

Step 1: Calculate the standard enthalpy and entropy changes:

ΔH° = $\Delta Hf° (H_2O_{(g)}) - \Delta Hf° (H_2O_{(l)}) = [-241.82 \text{ kJ/mol} - (-286.83 \text{ kJ/mol})] = 45.01 \text{ kJ}$

ΔS° = $1\text{mol} \times S°(H_2O_{(g)}) - 1\text{mol} \times S°(H_2O_{(l)}) = (1 \text{ mol})188.8 \text{J/mol·K} - (1 \text{ mol})70.0 \text{J/mol K} = 118.8 \text{J/K}$

Step 2: Substitution into the standard free energy equation yields:

$\Delta G° = \Delta H° - T\Delta S°$

ΔG° $= \Delta H° - T\Delta S° = 45.01 \text{ kJ} - (298 \text{ K} \times 118.8 \text{ J/K}) \times 1 \text{ kJ } (1000 \text{ J})$

$= 45.01 \text{ kJ} - 35.4 \text{ kJ} = 9.6 \text{ kJ}$

At 298 K (25 °C) $\Delta G° > 0$, so boiling is nonspontaneous (*not* spontaneous).

C. Using Standard Free Energy of Formation ($\Delta G_f°$) to calculate ΔG°:

The standard free energy change for a reaction **(ΔG°)** may also be calculated from Standard Free Energy of Formation ($\Delta G_f°$) values of the reactants and products involved in the reaction.

- **The Standard Free Energy of Formation ($\Delta G_f°$)** is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. The approach used to calculate ΔG° for a reaction from **($\Delta G_f°$)** values is the same as that demonstrated previously for enthalpy and entropy changes.

- **The Standard Free Energy Change (ΔG°)** at room temperature may be calculated as

$$\Delta G° = \sum n\Delta G°f_{(products)} - \sum n\Delta G°f_{(reactants)}$$

EXAMPLE:

1. Consider the decomposition of yellow mercury(II) oxide.

$HgO_{(s,yellow)} \longrightarrow Hg_{(l)} + 12O_{2(g)}$

- Calculate the standard free energy change at room temperature, ΔG°, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?
-

Solution:
The required data are available as:

Compound	ΔG°f (kJ/mol)	ΔH°f (kJ/mol)	S° (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

a. Using Free Energies of Formation:

$$\begin{aligned}\mathbf{\Delta G°} &= \sum n\Delta G°f_{(products)} - \sum n\Delta G°f_{(reactants)}\\ &= [1\ \Delta G°f\ Hg_{(l)} + 12\ \Delta G°f\ O_{2(g)}] - 1\Delta G°f\ HgO_{(s,yellow)}\\ &= [\ 1mol\ (0\ kJ/mol) + 12mol\ \ (0\ kJ/mol)\ ] - 1\ mol\ (\ -58.43\ kJ/mol\ ) = \mathbf{58.43\ kJ/mol}\end{aligned}$$

b. Using Enthalpies And Entropies of Formation:

$$\begin{aligned}\mathbf{\Delta H°} &= \sum n\Delta H°f\ (products) - \sum n\Delta H°f\ (reactants)\\ &= [1\ \Delta Hf°\ Hg(l) + 12\ \Delta Hf°\ O_{2(g)}] - 1\ \Delta Hf°\ \ HgO_{(s,yellow)}\\ &= [1\ mol(0\ kJ/mol) + 12mol\ (0\ kJ/mol)] - 1\ mol\ (\ -90.46\ kJ/mol\ ) = \mathbf{90.46\ kJ/mol}\end{aligned}$$

$$\begin{aligned}\mathbf{\Delta S°} &= \sum n\Delta S°_{(products)} - \sum n\Delta S°_{(reactants)}\\ &= [1\ \Delta S°\ Hg_{(l)} + 12\Delta S° O_{2(g)}\ ] - 1\Delta S°\ HgO_{(s,yellow)}\\ &= [1mol(75.9\ J/molK) + 12mol\ (205.2\ J/molK)\ ] - 1mol(71.13\ J/molK) = \mathbf{107.4\ J/mol\ K}\end{aligned}$$

Therefore: Using the derived values:

$$\begin{aligned}\mathbf{\Delta G°} &= \Delta H° - T\Delta S°\\ &= 90.46\ kJ - 298.15\ K \times 107.4\ J/K\cdot mol \times 1\ kJ\ /\ 1000\ J\\ &= 90.46\ kJ - 32.01\ kJ/mol = \mathbf{58.45\ kJ/mol}\end{aligned}$$

- Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (*not* spontaneous) at room temperature.

D. Free Energy Changes (ΔG°) for Coupled Reactions

The approach is analogous to the use of Hess' Law in computing enthalpy changes. Consider the vaporization of water as an example:

$$\mathrm{H_2O}(l) \rightarrow \mathrm{H_2O}(g)$$

An equation representing this process may be derived by adding the formation reactions for the two phases of water (necessarily reversing the reaction for the liquid phase). The free energy change for the sum reaction is the sum of free energy changes for the two added reactions:

$$\begin{array}{ll} \mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightarrow \mathrm{H_2O}(g) & \Delta G^\circ_\mathrm{f}\mathrm{gas} \\ \underline{\mathrm{H_2O}(l) \rightarrow \mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g)} & \underline{-\ \Delta G^\circ_\mathrm{f}\mathrm{liquid}} \\ & \\ \mathrm{H_2O}(l) \rightarrow \mathrm{H_2O}(g) & \Delta G^\circ = \Delta G^\circ_\mathrm{f}\mathrm{gas} - \Delta G^\circ_\mathrm{f}\mathrm{liquid} \end{array}$$

This approach may also be used in cases where a nonspontaneous reaction is enabled by coupling it to a spontaneous reaction.

For example, the production of elemental zinc from zinc sulfide is thermodynamically unfavorable, as indicated by a positive value for ΔG°:

$$\mathrm{ZnS}(s) \rightarrow \mathrm{Zn}(s) + \mathrm{S}(s) \qquad \Delta G^\circ_1 = 201.3\,\mathrm{kJ}$$

The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:

$$\mathrm{S}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{SO_2}(g) \qquad \Delta G^\circ_2 = -300.1\,\mathrm{kJ}$$

The coupled reaction exhibits a negative free energy change and is spontaneous:

$$\mathrm{ZnS}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{Zn}(s) + \mathrm{SO_2}(g) \qquad \Delta G^\circ = 201.3\,\mathrm{kJ} + -300.1\,\mathrm{kJ} = -98.8\,\mathrm{kJ}$$

This process is typically carried out at elevated temperatures, so this result obtained using standard free energy values is just an estimate.

Example:

Calculating Free Energy Change for a Coupled Reactions

A reaction coupling the decomposition of ZnS to the formation of H_2S expected to be spontaneous under standard conditions?

Solution: Following the approach outlined above and using free energy values

$$\begin{array}{lll} \text{Decomposition of zinc sulfide:} & \mathrm{ZnS}(s) \rightarrow \mathrm{Zn}(s) + \mathrm{S}(s) & \Delta G^\circ_1 = 201.3\,\mathrm{kJ} \\ \text{Formation of hydrogen sulfide:} & \mathrm{S}(s) + \mathrm{H_2}(g) \rightarrow \mathrm{H_2S}(g) & \Delta G^\circ_2 = -33.4\,\mathrm{kJ} \\ \text{Coupled reaction:} & \mathrm{ZnS}(s) + \mathrm{H_2}(g) \rightarrow \mathrm{Zn}(s) + \mathrm{H_2S}(g) & \Delta G^\circ = 201.3\,\mathrm{kJ} + -33.4\,\mathrm{kJ} = 167.9\,\mathrm{kJ} \end{array}$$

The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

E. Free Energy and Equilibrium.

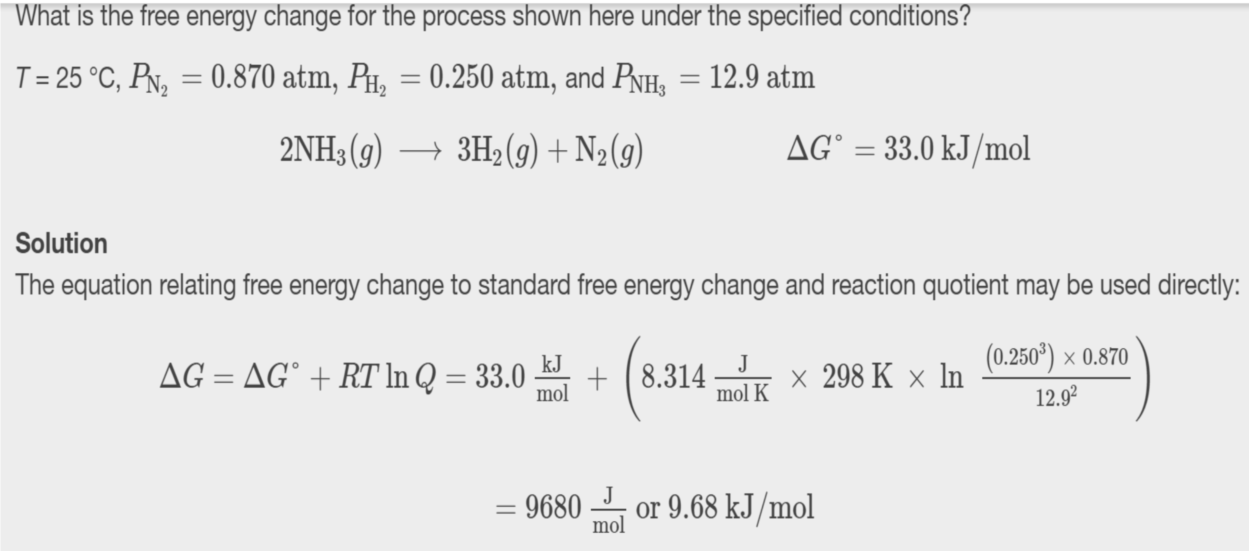
1. Non-Standard Condition: (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change according to this equation:

$$\Delta G = \Delta G° + RT\ \mathrm{In}Q$$

Where: R is the gas constant (8.314 J/K mol),
T is the kelvin or absolute temperature, and
Q is the reaction quotient.

- For gas phase equilibria, the pressure-based reaction quotient, Q_P, is used. The concentration-based reaction quotient, Q_C, is used for condensed phase equilibria.
-

Example:
Calculating Δ*G* under Nonstandard Conditions



What is the free energy change for the process shown here under the specified conditions?

T = 25 °C, $P_{N_2} = 0.870\ \mathrm{atm}$, $P_{H_2} = 0.250\ \mathrm{atm}$, and $P_{NH_3} = 12.9\ \mathrm{atm}$

$$2NH_3(g) \longrightarrow 3H_2(g) + N_2(g) \qquad \Delta G^\circ = 33.0\ \mathrm{kJ/mol}$$

Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$\Delta G = \Delta G^\circ + RT\ln Q = 33.0\ \frac{\mathrm{kJ}}{\mathrm{mol}} + \left(8.314\ \frac{\mathrm{J}}{\mathrm{mol\ K}} \times 298\ \mathrm{K} \times \ln\ \frac{(0.250^3)\times 0.870}{12.9^2}\right)$$

$$= 9680\ \frac{\mathrm{J}}{\mathrm{mol}}\ \text{or}\ 9.68\ \mathrm{kJ/mol}$$

2. System at Equilibrium Condition: *Q* = *K* and Δ*G* = 0, and the previous equation may be written as

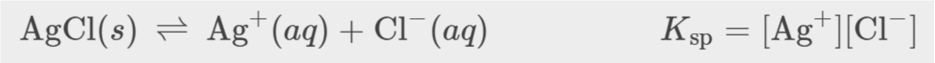
$$0 = \Delta G^\circ + RT\ln K \qquad \text{(at equilibrium)}$$

$$\Delta G^\circ = -RT\ln K \qquad \text{or} \qquad K = e^{-\frac{\Delta G^\circ}{RT}}$$

Example:
Calculating an Equilibrium Constant using Standard Free Energy Change,
Given that the Standard Free Energies of Formation of $Ag^+(aq)$, $Cl^-(aq)$, and AgCl(*s*) are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution:

The reaction of interest is the following:



$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\Delta G^\circ = [\Delta G^\circ_f(\mathrm{Ag^+}(aq)) + \Delta G^\circ_f(\mathrm{Cl^-}(aq))] - [\Delta G^\circ_f(\mathrm{AgCl}(s))]$$
$$= [77.1\ \mathrm{kJ/mol} - 131.2\ \mathrm{kJ/mol}] - [-109.8\ \mathrm{kJ/mol}] = 55.7\ \mathrm{kJ/mol}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol{\cdot}K} \times 298.15\ \mathrm{K}}\right)$$

$= \exp(-22.470) = e^{-22.470} = \mathbf{1.74 \times 10^{-10}}$

Activities and Assessment:

1. Use standard enthalpy and entropy data value from the Table**:** to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for Δ*G*° say about the spontaneity of this process?

$C_2H_{6(g)} \longrightarrow H_{2(g)} + C_2H_{4(g)}$

2. Calculate Δ*G*° using (a) free energies of formation and (b) enthalpies of formation and entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$C_2H_{4(g)} \longrightarrow H_{2(g)} + C_2H_{2(g)}$

3. What is the standard free energy change for the reaction below? Is the reaction expected to be spontaneous under standard conditions?

$FeS_{(s)} + O_{2(g)} \rightarrow Fe_{(s)} + SO_{2(g)}$

4. Use the thermodynamic data provided value from the Table**:** to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

5.Given the following reactions:

$$\mathrm{P_4}(s) + 5\mathrm{O_2}(g) \longrightarrow \mathrm{P_4O_{10}}(s) \qquad \Delta G^\circ = -2697.0\ \mathrm{kJ/mol}$$
$$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{H_2O}(g) \qquad \Delta G^\circ = -457.18\ \mathrm{kJ/mol}$$
$$6\mathrm{H_2O}(g) + \mathrm{P_4O_{10}}(s) \longrightarrow 4\mathrm{H_3PO_4}(l) \qquad \Delta G^\circ = -428.66\ \mathrm{kJ/mol}$$

(a) Determine the standard free energy of formation, **ΔG°**f, for phosphoric acid.
(b) How does your calculated result compare to the constant thermodynamic value from the table? Explain.

6. Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction:

$$2\mathrm{H_2S}(g) + \mathrm{SO_2}(g) \rightleftharpoons \tfrac{3}{8}\mathrm{S_8}(s,\ \mathrm{rhombic}) + 2\mathrm{H_2O}(l)$$

What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

7. Determine the standard free energy change, ΔGf°, for the formation of $S^{2-}_{(aq)}$ given that the ΔGf° for $Ag^{+}_{(aq)}$ and $Ag_2S_{(s)}$ are 77.1 kJ/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S_{(s)}$ is $8 \times\times 10^{-51}$.

8. A reaction has ΔH° = 100 kJ/mol and ΔS°=250 J/mol·K. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

LESSON 05: HEAT ENGINES
Unit 01: Introduction to Heat Engines

Introduction:

Heat engines are machines that operate continuously, producing Work from the heating value of fuels. Its importance cannot be understated in our world today and the future, for we rely so much in this process in order to propel our industries to greater heights. Heat engines and the second law of thermodynamics had had their histories tied with each other, and in this module, we discover the basic thermodynamics on the engine processes while also revisiting related concepts leading to the formulation of the second law and Entropy. In particular, we will discuss the Carnot process and discuss the principles on how it idealized the maximum efficiency possible in the conversion of heat into work by engines.

Learning Objectives:

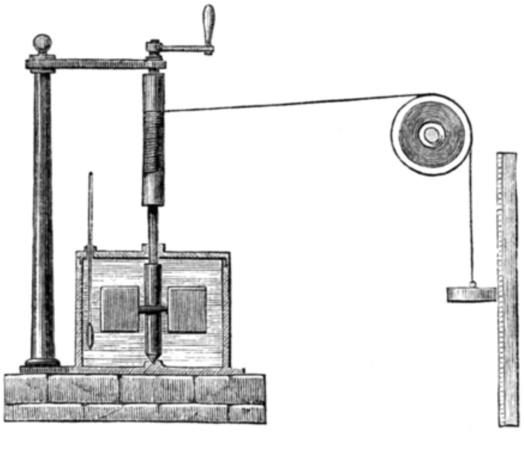
After successful completion of this chapter, the students are expected to:

1.) Construct the energy balances used in the conversion of Heat to Work to define the efficiency of engines.
2.) Distinguish the different features of the Reversible Process and appraise their importance towards constructing an ideal engine.
3.) Examine the parts of the Carnot Process and how it led to the definition of maximum engine efficiency.

Course Material:

Conversion of Heat to Work

In 1843, a classic experiment by James Joule used the change in potential energy of falling masses to stir water. The water temperature increased, much like it would when put over a flame. Joule found that the amount of mechanical work needed to raise the temperature of 1 pound of water by 1-degree Fahrenheit was a consistent value of 778.24-foot pound force (4.1550 J·cal−1). He contended that motion and heat were mutually interchangeable and that, in every case, a given amount of work would generate the same amount of heat. Today this important physical observation is known as the Mechanical Equivalent of Heat, stating that that Mechanical energy can be converted into heat, and heat can be converted into some mechanical energy.



In terms of the First Law of Thermodynamics, the mechanical Equivalent of Heat implies that one can change the Internal energy (U) of a system by either doing work (W) to the system, or adding heat (Q) to the system.

$$dU = Q + W$$

In Joule's experiment, work was done to raise the internal energy of the water, and this is without adding heat (Q=0); an adiabatic process assuming that no heat was lost to the instrument components nor friction to its moving parts.

$$dU = 0 + W$$

@V = k (incompressible liquids); $dU = C_v dT$

$$C_v dT = W$$

As of the equation above, the temperature change (dT) of the liquid from the work done (W). Joule was quite successful because his value of 4.1550 J·cal−1 was close to modern value of the specific heat of water. However, conversion of Work to Heat is just one path. The more interesting inquiry is whether we could attain the same level of precision and success when converting Heat into useful Work; could we efficiently convert the heat from burning Fuels into industrial work?

In turns out that this is not the case, because all efforts to devise a process for continuous conversion of heat completely into work or into mechanical or electrical energy have failed. Regardless of improvement, the heat-to-work conversion efficiencies do not exceed 40%. Within that experience, the second law which have led to the concept of Entropy has this for its first statement: "No apparatus can operate in such a way that is only effect is to convert heat absorbed by a system completely into work done by the system."

$$QH = QC + W$$
$$W = QH - QC$$

In equation form as seen above, we see that for every W attempted to be generated from QH, a discarded heat of QC is required. Engines which attempt to do this job has their efficiencies described using these parameters.

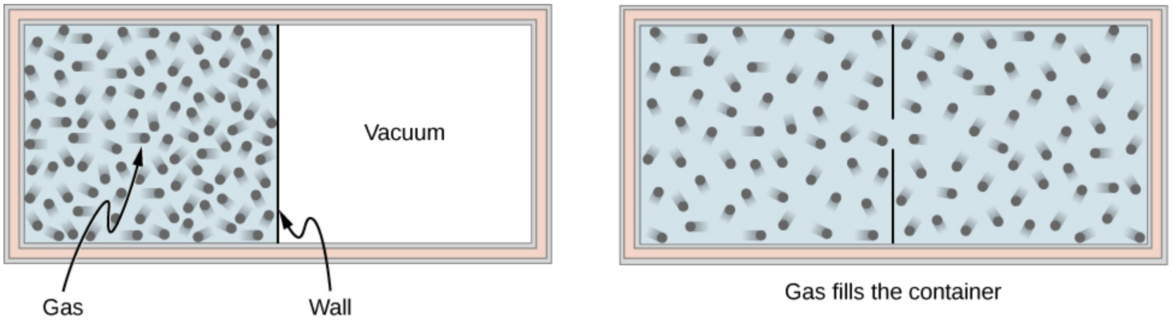
$$\eta = \frac{W}{Q_H} \text{ or } \eta = 1 - \frac{Q_C}{Q_H}$$

As we have stated earlier, engineering experience tells us that the efficiency (η) of engines are only limited to 40% (η =0.4). This means that almost 60% of QH thrown away as exhaust heat QC.

So how do we construct the perfect engine with the greatest efficiency? In here we discuss the Carnot Engine or the Carnot process which has the maximum efficiency for any heat-to-work converting Engine.

The Reversible Process

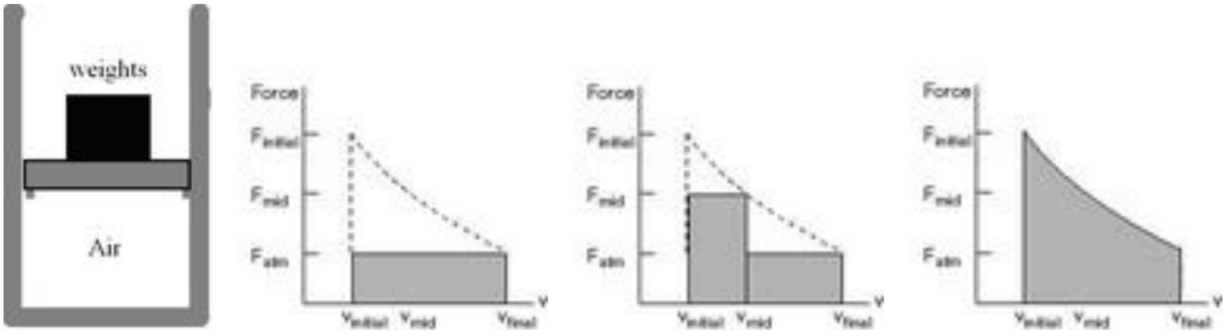
First, we need our ideal Engine to be "Reversible", which is quite a difficult restriction in itself. Basically, a process is "reversible" when the system and environment can be restored to exactly the same initial states that they were before the process occurred, after one goes backward along the path of the said process. But to understand this concept and why it is required in building maximum efficiency engines, we will break down each facet of the reversible condition.



(a) (b)

As on the figure above, we consider an ideal gas that is held in half of an insulated container with a wall in the middle. The other half of the container is under vacuum with no molecules inside. Now, if we remove the wall in the middle quickly, the gas expands and fills up the entire container immediately, as shown in the right side of the above figure. Now, can all the molecules go backward to the original half of the container in some future time? Our intuition tells us that this is going to be very unlikely. Even though nothing prevents such an event from happening, we intuitively know how small the probability for that event is.

What we are really asking in this line of reasoning is whether this expansion process is reversible or not. And we know that this process is NOT reversible because the probability is very low and unlikely. In terms of the Boltzmann definition of Entropy, state (b) has a higher entropy than state (a). Therefore, event (a) to (b) is spontaneous because it increases the change of entropy of the system but event (b) to (a) will not be spontaneous because that will decrease the entropy of the system. The first reason why reversible process remains an ideality is that because natural, spontaneous process favor high entropies. However, for a process to become spontaneous, the entropy of the system and surroundings must total to zero.



The second point to elaborate is why zero entropy is important for the construction of maximum efficiency engines. For this we consider another system where we have a thermally insulated cylinder that holds an ideal gas. The gas is contained by an insulated and massless piston with a stack of many small weights on top of it.

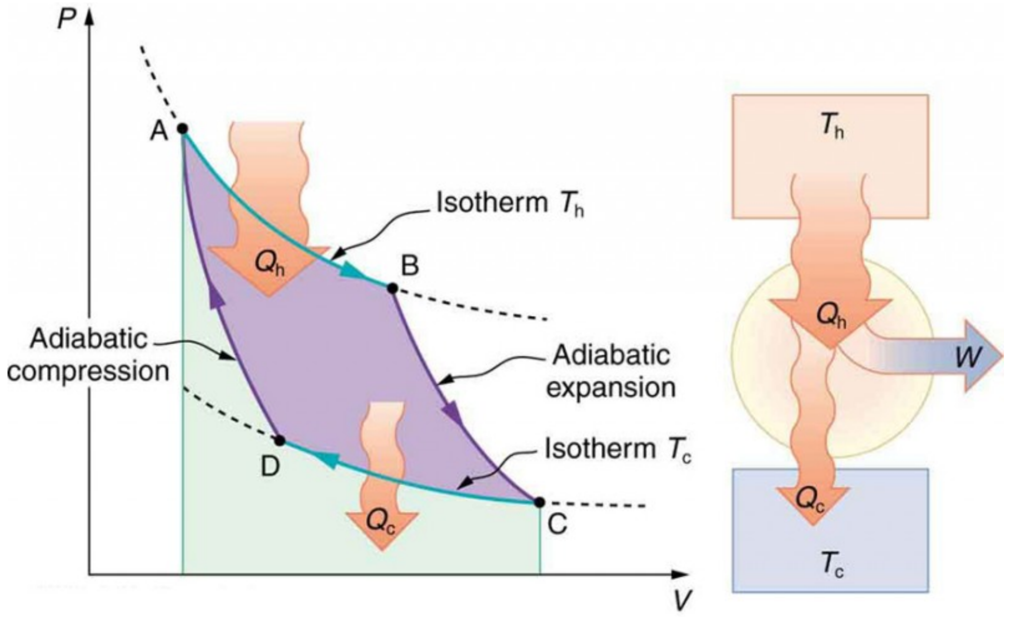
Initially the system is in mechanical and thermal equilibrium. But depending on how we remove the weights above the piston, we could get different values of work from this compressed gas as we see in the graphs above. The first graph happens when we instantly remove all the weights, and we see that by doing this we not getting a very large area in our Work integral. The second graph results from removing half of the weight, waiting for the system to achieve equilibrium, before finally removing the remaining half. We see that removing the weight partially and waiting for equilibrium results to a higher work value than the first. If we remove the weights infinitesimally, one at a time, waiting for equilibrium each time, this would result to the maximum work possible. However, getting this maximum value out of our system is very unlikely because that process takes too long happen. What happens is a trade-off, waiting for equilibrium and moving infinitesimally is slow but will give us maximum work. Meanwhile, increasing the driving force instantaneously is less efficient but will result to a faster process. The "lost work" associated with choosing the faster process becomes the Entropy of choosing that process. Zero Entropy is achieved if we have chosen to wait for equilibrium at each infinitesimal driving force set for the whole process instead.

This "lost work" that generates Entropy in irreversible processes is also known as the phenomenon of Dissipation, or the energy we give to the environment that increase its Entropy. From our piston-weighs set-up, we see that proceeding the non-infinitesimal route would result to lesser work extracted from the system. Unfortunately, if we do not use small increments and wait for equilibria in each step, it will be hard for us to direct all the energy to the conversion of heat into work. For the piston set-up, dissipation may result into friction, or into sound and vibration or the transfer of heat into the surroundings. All of these Entropy increasing processes to the environment could have not occurred if we had just proceeded slowly, gradient by gradient in equilibrium – which is often not the case.

Lastly, note that even though it is possible to restore a system to its original state; the hard part is to have its environment also restore to its original state at the same time. For example, in the example of an ideal gas expanding into twice its original volume, one can easily push it back with a piston and restore its temperature and pressure by removing some heat from the gas. The problem is that doing this will still change something in its surroundings, such as dumping some heat outside the system; as we have seen with our equations on heat engines. A reversible process is therefore an ideal process that rarely happens, and in reality, almost all processes are irreversible.

Maximum Efficiency with Carnot Engines

We will now use the points discussed on heat conversion, efficiency and reversibility in constructing the Carnot Engine (or Carnot Process) which claims to have the highest efficiency in when converting heat to work. On the figure below we show the Carnot Process with its PV diagram to the left and its schematic diagram on the right.



On the PV diagram we see the process path A-B-C-D with four processes in a closed loop. This means that it is a Cyclic process, that starts and returns on the same points, just as we observe all engines working continuously on operation. A-B and C-D are isothermal processes, while B-C and D-A are adiabatic processes. Qh and Qc are heat input at Th and heat exhausted to Tc respectively, while the enclosed area is the work to be generated by this cyclic process.

To maximize the work, we get from the process, we follow what we have discussed in the concept of reversibility. Th and Tc are the driving force for heat flow this time, and for the idealized Carnot process we set Th and Tc into Heat Reservoirs, meaning that their temperature values don't change despite the transfer of heat. Since Th and Tc are fixed, this serves the same purpose as the infinitesimal differences (+dT); serving as a work-around by eliminating the temperature gradient we were previously concerned with. This is done by only allowing two temperatures Th and Tc throughout the whole process, without in-between values, and thus we have nothing to dissect infinitesimally.

We start the cycle in process A-B, where the gas expands isothermally at Th, ensuring that all the Qh entering the system at this point is being translated to a pressure-volume work by our fluid. The adiabatic expansion in process B-C again makes the gas work through expansion while ensuring that no heat escapes the system as it approaches the exhaust temperature, Tc. Process C-D shows the requirement of ejecting Qc at Tc in every process trying to convert heat into work. Process C-D is a compression step, meaning that compressive work is being done towards the fluid instead of being generated by the fluid itself. The last step before repeating the cycle is process D-A which allows the system to again approach the higher fuel temperature, Th, as it tries again to convert input Qh into useful expansion work by the fluid.
These steps and the reversible design of the Carnot Process ensures that no energy is being dissipated unnecessarily by the system. Remember that even though Qc is a discarded heat, it is also a requirement and thus necessary in every heat-to-work conversion. Thus, the Carnot Process is an optimized idealization of the upper limit of what more practical engines could actually achieve. To get the Carnot efficiency of a process we modify the previous efficiency formula into:

$$\eta_{\text{carnot}} = 1 - \frac{T_C}{T_H}$$

Now we could use this upper-limit efficiency that is only dependent on temperature in evaluating efficiency claims of other heat-to-work processes.

SAMPLE PROBLEM:

For a coal fired utility boiler, the temperature of high-pressure steam would be about 540 degrees C and Tcold, the cooling tower water temperature, would be about 20 degrees C. Calculate the Carnot efficiency of the power plant. What is the maximum energy that we could get from the powerplant, given that the amount of coal used was equivalent to 150 Mega Joules of heat?

Step 1: Convert the high and low temperatures from Celsius to Kelvin:

Thot = 540^{o}C+273 = 813K
Tcold = 20^{o}C+273 = 293K

Step 2: Determine the efficiency using the Carnot efficiency formula:

η_{carnot}=[1−Tcold/ Thot]×100%
η_{carnot}=[1−293K/813K]×100%=64%

From the Carnot Efficiency formula, it can be inferred that a maximum of 64% of the fuel energy can go to generation. To make the Carnot efficiency as high as possible, either T_{hot} should be increased or T_{cold} (temperature of heat rejection) should be decreased.

Step 3: Use the efficiency and fuel value to find the maximum output of the plant:
W = η*Qh/100
W = 64*150 MJ/100 = 96MJ

Activities/Assessments:

1. An egg, initially at rest, is dropped onto a concrete surface; it breaks. Prove that the process is irreversible. In modeling this process treat the egg as the system, and assume the passage of sufficient time for the egg to return to its initial temperature.
2. Which is the more effective way to increase the thermal efficiency of a Carnot engine; to increase Th with Tc constant, or to decrease Tc with Th constant? For a real engine, which would be the more practical way?
3. A Carnot Engine receives 250 KJ/s of heat from a heat-source reservoir at 525 C and rejects heat to a heat-sink reservoir at 50 C. What is the power developed and heat rejected?

4. The following heat engines produce power of 95, 000 kW. Determine in each case the rates at which heat is absorbed from the hot reservoir and discarded to the cold reservoir.
a. A Carnot engine operates between heat reservoirs 750K and 300K
b. A practical engine operates between the same heat reservoirs but with a thermal efficiency η = 0.35

5. An inventor claims to have devised a cyclic engine which exchanges heat with reservoirs 25C and 250 C, and which produces 0.45 kJ of work for each kJ of heat extracted from the hot reservoir. Is the claim believable?

LESSON 7: NUCLEAR CHEMISTRY
UNIT 1: Definitions in Nuclear Chemistry

Introduction:

Before we delve deeper into nuclear chemistry, a clarification of terms used in nuclear science is in order. Many terms have similar uses but have different meanings when they are correctly defined. This is also to help remove the confusion when using these terms.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Define common terms used in nuclear chemistry.
2. Describe particles involved in a nuclear reaction.

Course Materials:

Nuclear reactions are reactions that involve the changes of atoms from one element, to atoms of another element. This could be achieved by either letting an unstable isotope release its energy along with other particles to achieve stability, or an element is bombarded by a particle, thereby inducing changes in its nucleus.

This concept is very sought after, especially in the medieval times where alchemists sought after what is called as the **philosopher's stone**; an object that will be able to change one element into another. These alchemists already thought that mercury would be the element that will transmute into gold, a very prized element in those times, and tried a lot of things to do this conversion. Modern alchemists have already done that through nuclear reactions (yet are unable to commercialize it since the process of conversion is very expensive as compared to the price of the yielded metal).

$$
\begin{gathered}
{}^{196}_{80}\mathrm{Hg} + \mathrm{n}^0 \rightarrow {}^{197}_{80}\mathrm{Hg} + \gamma \\
{}^{197}_{80}\mathrm{Hg} + \mathrm{e}^- \rightarrow {}^{197}_{79}\mathrm{Au} + \mathrm{v_e}
\end{gathered}
$$

These nuclear reactions are the basis of a sub-branch of chemistry called **nuclear chemistry**. The term nuclear is derived from the nucleus, in which most of these changes are involved. This branch also deals with other terms that are important to remember.

Nuclear decay is a nuclear reaction in which an unstable isotope of an element (a **radioisotope**) disintegrates into a more stable form, releasing energy via radiation. These disintegrations would be further discussed in the text.

Nuclear radiation is the transmission of energy from a nuclear reaction, through space, or even through some sort of material. Some of these radiations could penetrate through walls.

Nuclear reactions have a bad reputation because of the usage of the nuclear bombs during World War II, and the accidents that happened on several nuclear reactors, most notably the Chernobyl reactor. Most of the problems encountered in the past have already been addressed and improved upon nowadays, and nuclear energy is now one of the more desirable alternative energies; it is relatively clean, it's yield is more favorable as compared to other sources of energy, and is relatively cheaper (it has a high building cost, but has very low maintenance cost) compared to other common sources. A comparison of costs of nuclear energy to other forms is shown in **Figure 1**.

Nuclear reactions involve particles that are otherwise not seen in standard chemical reactions. **Table 1** shows the common particles and subatomic particles involved in a nuclear reaction. This is shown so to avoid confusion in the text. Familiarization on these terms would be useful in learning nuclear chemistry.

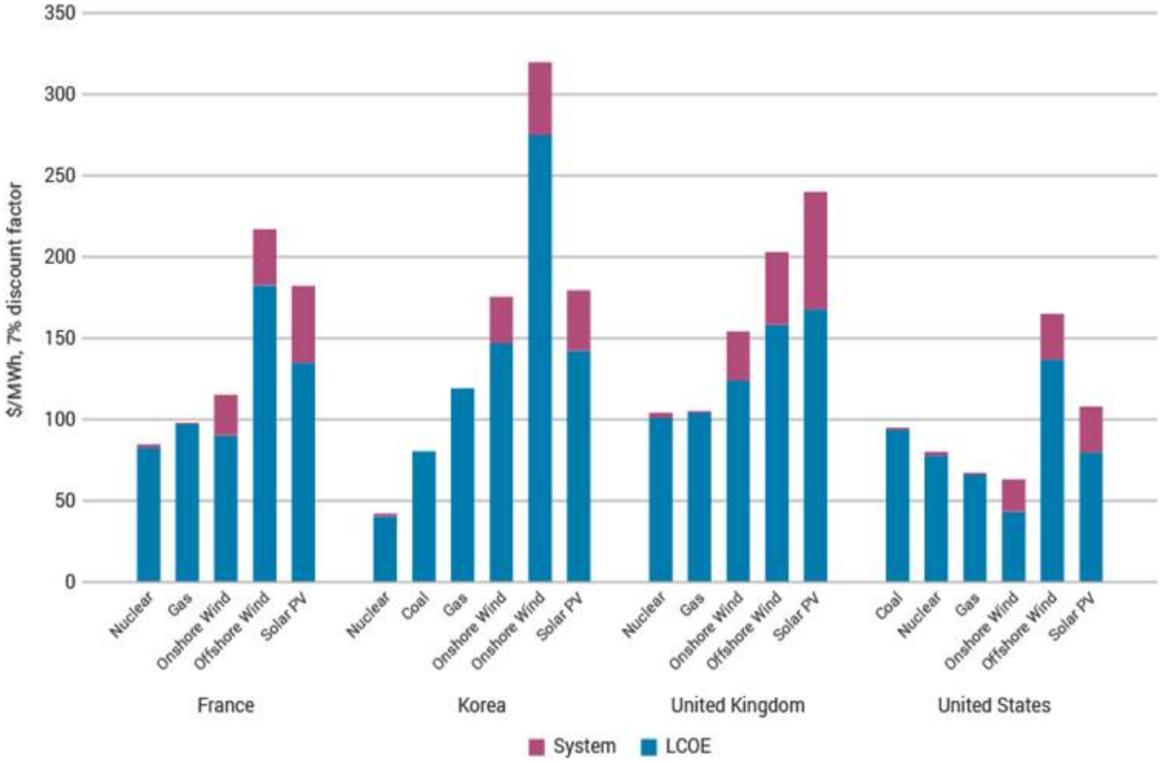


Figure 8 Comparative Levelized Costs of Electricity (LCOEs) and system costs in four countries (2014 and 2012). LCOE plant costs have been taken from Projected Costs of Generating Electricity 2015 Edition. System costs have been taken from Nuclear Energy and Renewables (NEA, 2012). A 30% generation penetration level for onshore wind, offshore wind and solar PV has been assumed in the NEA estimates of system costs, which include back-up costs, balancing costs, grid connection, extension, and reinforcement costs. A discount rate of 7% is used throughout, which is therefore consistent with the plant level LCOE estimates given in the 2015 edition of Projected Costs of Generating Electricity. The 2015 study applies a $30/t CO_2 price on fossil fuel use and uses 2013 US$ values and exchange rates. Taken from The World Nuclear Association website (https://www.world-nuclear.org/)

Table 1 List of particles involved in nuclear reactions. Also shown is a comparison of their masses and relative charges.

Particle	**Symbol**	**Mass (kg)**	**Rel. Charge (C)**
proton	p^+, ${}^{1}_{1}\mathrm{p}$	1.6726×10^{-27}	+1
neutron	n^0, ${}^{1}_{0}\mathrm{n}$	1.6749×10^{-27}	0
electron	${}^{0}_{-1}\mathrm{e}$, ${}^{0}_{-1}\beta$	9.1094×10^{-31}	–1

neutrino	ν_e	~0	0
antineutrino	$\bar{\nu}_e$	~0	0
alpha particle	α , $^{4}_{2}\mathrm{He}$	6.6447×10^{-27}	+2
positron	$^{0}_{1}\mathrm{e}$, $^{0}_{1}\beta$	9.1094×10^{-31}	+1
gamma ray	γ	0	0

Activities and Assessments:

1. Which of the following particles would attract each other? Would repel each other?
2. Rank the particles from most to least massive.
3. Using the comparison shown in Figure 1, would you advocate in the use of nuclear energy? Why or why not?

LESSON 7: NUCLEAR CHEMISTRY
UNIT 2: Types of Nuclear Decay

Introduction:

Nuclear decays are reactions that are spontaneous naturally. These types of reactions are the usual source of radioactivity that we get, albeit they usually give off small amounts of it in the public.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Describe the five common types of nuclear decay.
2. Predict the product of a nuclear decay reaction.

Course Materials:

There are five simple types of nuclear decay: alpha decay, beta decay, gamma decay, electron capture, and positron emission. Each of these reactions would be discussed in this part of the text.

Alpha decay is a nuclear reaction in which an alpha particle is ejected from a nucleus of a radioisotope. By doing so, the result would be a *nuclide with an atomic number decreased by two, and a mass number decreased by four*.

Examples:

$$^{149}_{64}\mathrm{Gd} \rightarrow {}^{145}_{62}\mathrm{Sm} + {}^{4}_{2}\mathrm{He}$$
$$^{232}_{90}\mathrm{Th} \rightarrow {}^{228}_{88}\mathrm{Ra} + {}^{4}_{2}\mathrm{He}$$
$$^{210}_{86}\mathrm{Rn} \rightarrow {}^{206}_{84}\mathrm{Sm} + {}^{4}_{2}\mathrm{He}$$

In general, for an alpha decay:

$$^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\mathrm{He}$$

where X is the element symbol corresponding to the atomic number Z and X' is the element symbol corresponding to the atomic number $\mathrm{Z}-2$.

Sample Problem 1

Predict the resulting nuclide when $^{222}_{88}\mathrm{Ra}$ undergoes alpha decay. Show also the complete nuclear reaction.

- Since we know that an alpha decay would result in a nuclide with $\mathrm{Z}-2$ and $\mathrm{A}-4$, we have:

$$\mathrm{Z}-2 = 88-2 = 86$$
$$\mathrm{A}-4 = 222-4 = 218$$

The element that has $Z = 86$ is Radon, so the resulting nuclide is $^{218}_{86}\mathrm{Rn}$. The complete reaction is

$$^{222}_{88}\mathrm{Ra} \rightarrow {}^{218}_{86}\mathrm{Rn} + {}^{4}_{2}\mathrm{He}$$

In a **beta decay**, a neutron decays into a proton and an electron. The electron is then emitted by the nucleus, and this emitted electron is now called as a **beta particle**, hence the symbol and the name. Additional studies about this reaction (as theorized by Wolfgang Pauli) has shown that another particle, with no charge and a very small mass that it was thought of before as zero mass, is emitted from a beta decay. This particle is called an **antineutrino**. Overall, the reaction would result in *an increase of one in the atomic number, while keeping the mass number intact*. This is due to the neutron converting into a proton, emitting both a beta particle and an antineutrino.

Examples:

$${}^{131}_{53}\mathrm{I} \rightarrow {}^{131}_{54}\mathrm{Xe} + {}^{0}_{-1}\beta + \bar{\nu}_\mathrm{e}$$
$${}^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\beta + \bar{\nu}_\mathrm{e}$$
$${}^{234}_{90}\mathrm{Th} \rightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\beta + \bar{\nu}_\mathrm{e}$$

In general, for a beta decay:

$${}^{A}_{Z}\mathrm{X} \rightarrow {}_{Z+1}^{\;\;A}\mathrm{X}' + {}^{0}_{-1}\beta + \bar{\nu}_\mathrm{e}$$

where X is the element symbol corresponding to the atomic number Z and X' is the element symbol corresponding to the atomic number $Z + 1$.

Sample Problem 2

Complete the following nuclear reaction:

$$? \rightarrow {}^{137}_{56}\mathrm{Ba} + {}^{0}_{-1}\beta + \bar{\nu}_\mathrm{e}$$

- For a beta decay, we keep A intact while increasing Z by one. However, since the original nuclide is missing, we must do the opposite. So, we need to subtract one from Z.

$$Z - 1 = 56 - 1 = 55$$

The element with $Z = 55$ is Cesium. So, the complete nuclear reaction is

$${}^{137}_{55}\mathrm{Cs} \rightarrow {}^{137}_{56}\mathrm{Ba} + {}^{0}_{-1}\beta + \bar{\nu}_\mathrm{e}$$

For a **gamma decay**, a high energy photon is released, which we call as a **gamma ray**. This usually happens when a neutron in an excited state releases energy (in the form of the gamma ray) to achieve a ground state. *Gamma decay does not change both the atomic number and the mass number*. They usually accompany other types of decay, most notably beta decays of most nuclei. They can usually be omitted in writing a nuclear reaction.

In an **electron capture**, an electron in the first shell is captured by the nucleus. This in turn would convert one proton in the nucleus into a neutron. This would also release a non-charged, very small particle called a **neutrino**. Overall, this would result in a *decrease of one in the atomic number while keeping the mass number constant*, which is the opposite of a beta decay.

Examples:

$$ {}^{22}_{11}\mathrm{Na} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{22}_{10}\mathrm{Na} + \mathrm{v_e} $$
$$ {}^{67}_{31}\mathrm{Ga} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{67}_{30}\mathrm{Zn} + \mathrm{v_e} $$

In general, for an electron capture:

$$ {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}_{Z-1}^{A}\mathrm{X}' + \mathrm{v_e} $$

where X is the element symbol corresponding to the atomic number Z and X' is the element symbol corresponding to the atomic number $Z - 1$.

Sample Problem 3

If ${}^{18}_{9}\mathrm{F}$ could hypothetically do both electron capture and positron emission, what would be the nuclear reactions?

- For both these reactions, a decrease of 1 in Z would occur while A is constant. Therefore

$$ Z - 1 = 9 - 1 = 8 $$

The element Oxygen has $Z = 8$. So, writing the reactions:

Electron capture:

$$ {}^{18}_{9}\mathrm{F} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{18}_{8}\mathrm{O} + \mathrm{v_e} $$

Positron emission:

$$ {}^{18}_{9}\mathrm{F} \rightarrow {}^{18}_{8}\mathrm{O} + {}^{0}_{1}\beta + \mathrm{v_e} $$

Lastly, a **positron emission** happens when a proton in the nucleus decays into a neutron and a **positron**, which is then emitted out. This also yields a neutrino. Electron capture and positron emission have the same results: a *decrease of one in the atomic number while keeping the mass number constant*, although they have different mechanisms in doing so.

Examples:

$$ {}^{40}_{19}\mathrm{K} \rightarrow {}^{40}_{18}\mathrm{K} + {}^{0}_{1}\beta + \mathrm{v_e} $$
$$ {}^{83}_{38}\mathrm{Sr} \rightarrow {}^{67}_{37}\mathrm{Rb} + {}^{0}_{1}\beta + \mathrm{v_e} $$

In general, for a positron emission:

$$ {}^{A}_{Z}\mathrm{X} \rightarrow {}_{Z-1}^{A}\mathrm{X}' + {}^{0}_{1}\beta + \mathrm{v_e} $$

where X is the element symbol corresponding to the atomic number Z and X' is the element symbol corresponding to the atomic number $Z - 1$.

Additional Information

The antineutrino and the positron are examples of **antiparticles** in physics. Antiparticles are usually defined as having similar mass and spin compared to their counterparts (antineutrino is the antiparticle of a neutrino, while positron is the antiparticle of an electron), but with opposite charges. Some particles, like a photon, are their own antiparticle.

One particular trait of a particle – antiparticle pair is that when they collide, **annihilation** occurs. Annihilation produces other particles; in the case of an electron – positron annihilation,

$$ {}_{-1}^{0}\mathrm{e} + {}_{1}^{0}\mathrm{e} \rightarrow \gamma + \gamma $$

Activities and Assessments:

Write the nuclear equations for the following:

1. The beta decay of thorium–234
2. The alpha decay of radon–222
3. The positron emission of manganese–51
4. The electron capture of silver–106
5. The decay of bismuth–212 to polonium–212
6. The decay of radium–226 to radon–222
7. The decay of beryllium–7 to lithium–7

LESSON 7: NUCLEAR CHEMISTRY
UNIT 3: Kinetics of Nuclear Reactions

Introduction:

Studying the rate of our nuclear reactions would add to the understanding of their applications. Some of these nuclear reactions are very unstable and would disintegrate in a fraction of a second, while some have very long times before having a significant loss in amount.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Compute for the half – life or the decay constant of a nuclear reaction.
2. Apply the use of radioactivity to predict the amount of a sample to the emitted radiation of the sample.

Course Materials:

Radioactive decay always follows first order kinetics.

Recall

For the first order reaction of a single reactant, which is designated as A, the integrated rate law is

$$\ln\frac{[\mathrm{A}]_\mathrm{t}}{[\mathrm{A}]_0} = -\mathrm{kt} \Rightarrow \ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_\mathrm{t}} = \mathrm{kt}$$

or

$$[\mathrm{A}]_\mathrm{t} = [\mathrm{A}]_0 \mathrm{e}^{-\mathrm{kt}}$$

in which $[\mathrm{A}]_\mathrm{t}$ is the concentration of at a time t, while $[\mathrm{A}]_0$ is the initial concentration, and k is the rate constant.

A first order reaction would give a linear plot when $\ln[\mathrm{A}]_\mathrm{t}$ is plotted against t as shown in **Figure 2**.

Solving for the **half – life** (the time it takes for half of the substance to disintegrate):

$$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_{\mathrm{t}_{1/2}}} = \mathrm{kt}_{1/2} \Rightarrow \ln\frac{[\mathrm{A}]_0}{\frac{1}{2}[\mathrm{A}]_0} = \mathrm{kt}_{1/2} \Rightarrow \ln 2 = \mathrm{kt}_{1/2}$$

$$\mathrm{t}_{1/2} = \frac{\ln 2}{\mathrm{k}} \approx \frac{0.0693}{\mathrm{k}}$$

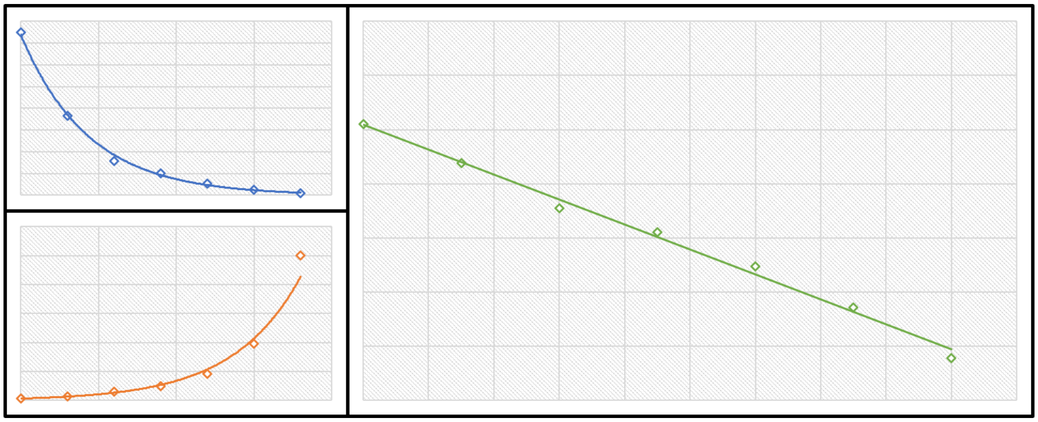


Figure 9 Simulated graphs of a first order reaction in a $[A]_t$ vs. t plot (top left), a $ln[A]_t$ vs. t plot (right), and a $1/[A]_t$ vs. t plot (bottom left). Notice the linearity in the right plot.

Sample Problem 4

Gold–198 ($^{198}_{79}\mathrm{Au}$) undergoes a beta decay to form stable $^{198}_{80}\mathrm{Hg}$. This reaction has a half – life of $2.697\ \mathrm{days}$.

a. What is the decay constant of gold–198?
b. When will a $25.00\ \mathrm{g}$ sample of gold–198 have a remaining mass of $10.00\ \mathrm{g}$?

- To obtain the decay constant, we use the formula

$$\mathrm{t}_{1/2} = \frac{\ln 2}{\mathrm{k}} \Longrightarrow \mathrm{k} = \frac{\ln 2}{\mathrm{t}_{1/2}}$$

$$\mathrm{k} = \frac{\ln 2}{2.697\ \mathrm{days}} = 0.2570\ \mathrm{day}^{-1}$$

- Applying the obtained rate constant, we can use

$$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_\mathrm{t}} = \mathrm{kt} \Longrightarrow \mathrm{t} = \frac{\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_\mathrm{t}}}{\mathrm{k}}$$

where $[\mathrm{A}]_\mathrm{t} = 10.00\ \mathrm{g}$, and $[\mathrm{A}]_0 = 25.00\ \mathrm{g}$.

$$\mathrm{t} = \frac{\ln\frac{25.00\ \cancel{\mathrm{g}}}{10.00\ \cancel{\mathrm{g}}}}{0.2570\ \mathrm{day}^{-1}} = 3.565\ \mathrm{days}$$

We could also apply the integrated rate law to the **activity** (R) of the sample. The activity of a sample is defined as the rate in which a sample decay. For nuclear activity, or radioactivity, we use the SI unit of **becquerel** (Bq), defined as one nucleus decaying per second. An older unit called the **curie** (Ci) is also used. The conversion of becquerels to curies is given by the following equation:

$$1\ \mathrm{Ci} = 3.7 \times 10^{10}\ \mathrm{Bq}$$

The integrated rate law is now transformed:

$$N = N_0 e^{-\lambda t}$$

in which N is the number of nuclei at time t, while N_0 is the initial number of nuclei, and λ is the decay constant.

The half – life equation is similar:

$$t_{1/2} = \frac{\ln 2}{\lambda} \approx \frac{0.0693}{\lambda}$$

The activity is defined as

$$R = \frac{\Delta N}{\Delta t}$$

and it can be shown that

$$R = \frac{N \ln 2}{t_{1/2}}$$

This equation is very con venient in some problems in nuclear chemistry.

Sample Problem 5

The Goiânia incident in Brazil happened in September 13, 1987 after a forgotten radiotherapy source was taken from an abandoned hospital site in the city. This source has an estimated radioactivity of $1400\ \mathrm{Ci}$ of ${}^{137}_{55}\mathrm{Cs}$ which then contaminated around 250 people and killed four. Given that the half – life of ${}^{137}_{55}\mathrm{Cs}$ is $30.2\ \mathrm{years}$, calculate the mass of ${}^{137}_{55}\mathrm{Cs}$ inside the source, in g. The molecular weight of ${}^{137}_{55}\mathrm{Cs}$ is $136.907089\ \mathrm{g/mol}$.

- Using the activity equation

$$\mathrm{R} = \frac{\mathrm{N}\ln 2}{\mathrm{t}_{1/2}} \Longrightarrow \mathrm{N} = \frac{\mathrm{Rt}_{1/2}}{\ln 2}$$

Substituting the given:

$$\mathrm{N} = \frac{1400\ \mathrm{Ci}(30.2\ \mathrm{years})}{\ln 2}$$

$$\mathrm{N} = \frac{1400\ \mathrm{Ci}\left(\frac{3.7\times10^{10}\ \mathrm{Bq}}{1\ \mathrm{Ci}}\right)(30.2\ \mathrm{years})\left(\frac{3.16\times10^{7}\mathrm{s}}{1\ \mathrm{year}}\right)}{\ln 2}$$

Note: $1\ \mathrm{Bq} = 1\ \mathrm{s}^{-1}$

$$\mathrm{N} = 7.13\times10^{22}$$

After obtaining N, we can now use Avogadro’s number and the molecular weight to obtain the mass:

$$\mathrm{particles} \xrightarrow{\mathrm{N_A}} \mathrm{moles} \xrightarrow{\mathrm{MW}} \mathrm{mass}$$

$$\mathrm{m} = 7.13\times10^{22}\ \mathrm{particles}\times\frac{1\ \mathrm{mol}}{6.022\times10^{23}\ \mathrm{particles}}\times\frac{136.907089\ \mathrm{g}}{1\ \mathrm{mol}}$$

$$\mathrm{m} = 1.62\ \mathrm{g}$$

Note: Imagine that few amounts had affected that many people, and even killed four. Compare that to the Chernobyl incident which registered approximately $6.00\ \mathrm{MCi}$, or around $70\ \mathrm{kg}$ of ${}^{137}_{55}\mathrm{Cs}$ (you can verify this by computation). No wonder there is stigma against nuclear energy. This is also not necessary the total amount in the container, but the amount that has possibly caused radiation by its decay. Sources say that here is about $93\ \mathrm{g}$ in the container but remember that ${}^{137}_{55}\mathrm{Cs}$ has a half – life of $30.2\ \mathrm{years}$.

Activities and Assessments:

1. When will a 1.00 g sample of thorium–232 have a mass of 1.00 mg, knowing that the half – life of thorium–232 is 1.405 × 10^{10} years?
2. A 1.00 L sample of water near a nuclear plant registered a 2.55 pCi of iodine–131. What is the concentration of iodine–131 is dissolved in the sample (in parts per million), given that the half – life of iodine–131 is 8 days, and its isotopic mass is 130.9061246 g/mol?
3. A sample of cobalt–60 was labelled as having an activity of 3.25 mCi, but upon inspection, it registers an activity of 1.50 × 10^7 Bq. How long ago did someone labelled the sample as having an activity of 3.25 mCi? Cobalt–60 has a half – life of 5.27 years, and has an isotopic mass of 59.9338222 g/mol.

LESSON 7: NUCLEAR CHEMISTRY
UNIT 4: Nuclear Stability

Introduction:

Most of the known isotopes are unstable, and experimentally, it has been proven that nuclear decays are a way to achieve stability. These experiments have been collected into what is known as a nuclide chart.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Predict if a nuclide is stable, or what type of decay it will undergo if unstable.
2. Describe a radioactive series using the nuclide chart.
4. Evaluate if a positron emission or a beta decay would happen in a given decay.

Course Materials:

Most of the known nuclides are unstable and would probably to radioactive decay until they achieve stability. Most experimental evidences of these radioactive decays and the stable nuclides are collected in what is called as a **chart of nuclides**. One such chart is shown in **Figure 3**.

The black area of the chart is defined as either the valley of stability, or the peninsula of stability. Every other colored marks around it is a member of the sea of instability. Some scientists define the top right dark areas that are separated to the other stable nuclides as the island of stability.

The other colors of the chart shows the preferred modes of decay of the unstable nuclides: ● yellow indicates an alpha decay, ● cyan indicates a beta decay, ● pink indicates a positron emission or an electron capture, ● light blue indicates a neutron emission, ● orange indicates a proton emission, ● green indicates spontaneous fission. Fission would be discussed at a later part of the module.

The chart of nuclides is used to predict what modes of decay would a given nuclide have.

For the chart, we could summarize the reactions as the following movements in the chart:
● yellow - alpha decay, go down twice and left twice
● cyan - beta decay, go up once and left once
● pink - positron emission or electron capture, go down once and right once
● orange - proton emission, go down once
● light blue - neutron emission, go left once

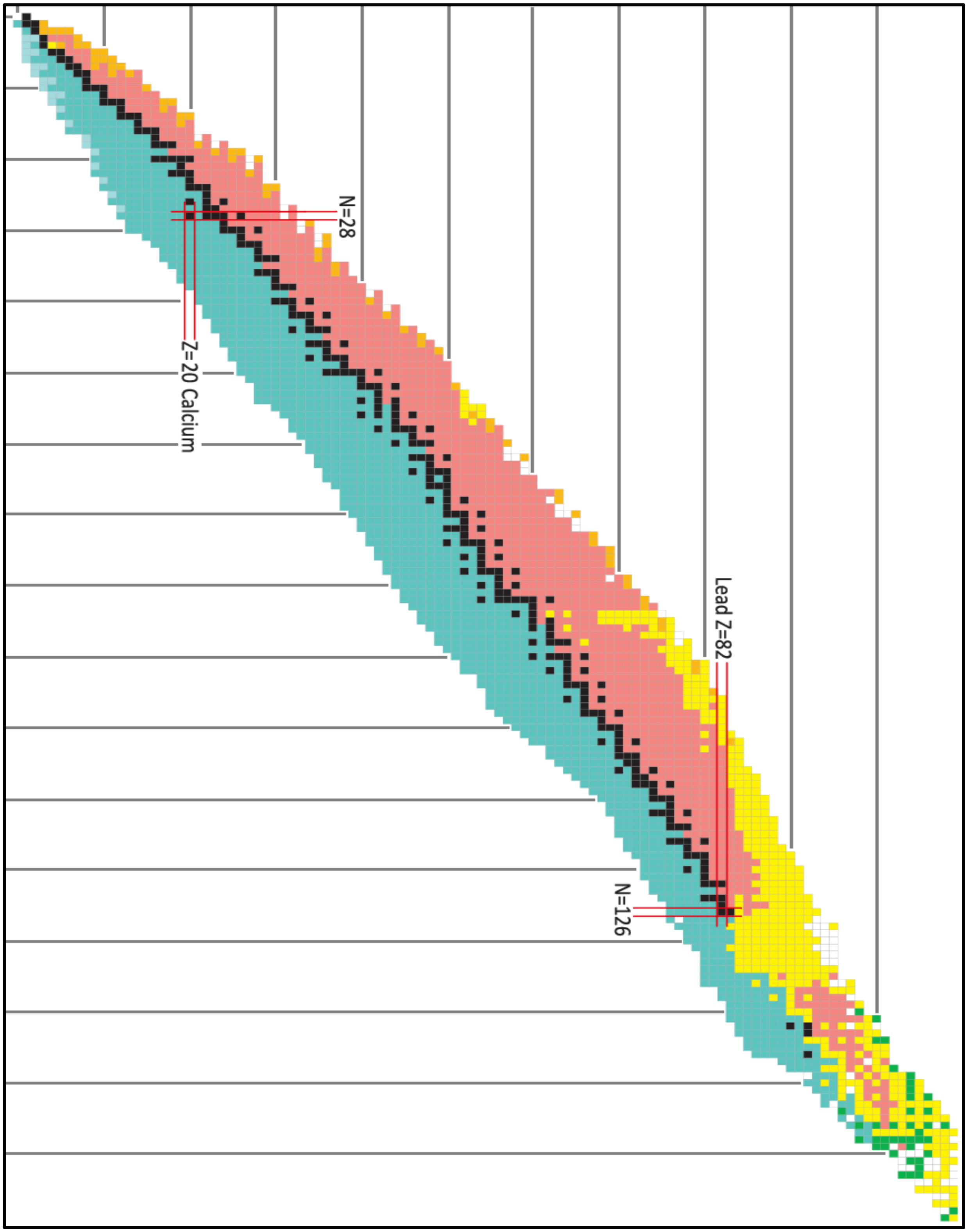


Figure 3 The Karlsruhe Nuclide Chart. The gray lines represent increments of ten, with the x-axis as the number of neutrons, while the y-axis is the number of protons. Calcium-48 and Lead-208 are shown as examples. Obtained from Sóti, Z., Magill, J., & Dreher, R. (2019). Karlsruhe Nuclide Chart – New 10th edition 2018. EPJ Nuclear Sciences & Technologies, 5, 6.

Sample Problem 6

Predict the mode of decay of the following nuclides.

a. Magnesium–23
b. Helium–5
c. Iodine–127
d. Neptunium–237

- For magnesium–23, ${}^{23}_{12}\mathrm{Mg}$, it has 12 protons and 11 neutrons. Locating this in the nuclide chart, we have a pink box, which indicates a positron emission or electron capture. The reaction would be

$${}^{23}_{12}\mathrm{Mg} \xrightarrow{\beta^{+}\ or\ \mathrm{e.c.}} {}^{23}_{11}\mathrm{Na}$$

- For helium–5, ${}^{5}_{2}\mathrm{He}$, it has 2 protons and 3 neutrons. Locating this in the nuclide chart, we have a light blue box, which indicates a neutron emission. The reaction would be

$${}^{5}_{2}\mathrm{He} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

- For iodine–127, ${}^{127}_{53}\mathrm{I}$, it has 53 protons and 74 neutrons. Locating this in the nuclide chart, we have a black box, which indicates that it is a stable nuclide. No decay is expected.

- For neptunium–237, ${}^{237}_{93}\mathrm{Np}$, it has 93 protons and 144 neutrons. Locating this in the nuclide chart, we have a yellow box, which indicates an alpha decay. The reaction would be

$${}^{237}_{93}\mathrm{Np} \rightarrow {}^{233}_{91}\mathrm{Pa} + {}^{4}_{2}\mathrm{He}$$

All these answers are seen in **Figure 4**.

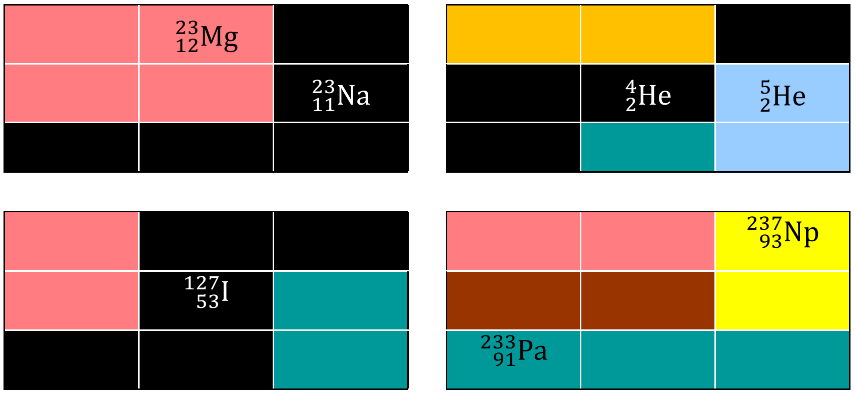


Figure 10 Nuclide Chart Diagrams: positron emission of magnesium–23 (top left), neutron emission of helium–5 (top right), stable iodine–127 (bottom left), and alpha decay of neptunium–237 (bottom right).

This chart can also be used to predict what we call as a **decay series**, reactions that unstable nuclides would react until a stable nuclide form.

Sample Problem 7

Write the whole decay series of Lutetium–151.

- Lutetium–151, $^{151}_{71}\mathrm{Lu}$, has 71 protons and 80 neutrons. In the nuclide chart, it is colored orange, suggesting a proton emission.

$$^{151}_{71}\mathrm{Lu} \rightarrow {}^{150}_{70}\mathrm{Yb} + {}^{1}_{1}\mathrm{p}$$

From $^{150}_{70}\mathrm{Yb}$ (70 protons, 80 neutrons), positron emissions or electron captures (pink boxes) would happen until $^{150}_{64}\mathrm{Gd}$.

$$^{150}_{70}\mathrm{Yb} \xrightarrow{\beta^+ \ or \ \text{e.c.}} {}^{150}_{69}\mathrm{Tm} + \mathrm{v_e}$$
$$^{150}_{69}\mathrm{Tm} \xrightarrow{\beta^+ \ or \ \text{e.c.}} {}^{150}_{68}\mathrm{Er} + \mathrm{v_e}$$
$$^{150}_{68}\mathrm{Er} \xrightarrow{\beta^+ \ or \ \text{e.c.}} {}^{150}_{67}\mathrm{Ho} + \mathrm{v_e}$$
$$^{150}_{67}\mathrm{Ho} \xrightarrow{\beta^+ \ or \ \text{e.c.}} {}^{150}_{66}\mathrm{Dy} + \mathrm{v_e}$$
$$^{150}_{66}\mathrm{Dy} \xrightarrow{\beta^+ \ or \ \text{e.c.}} {}^{150}_{65}\mathrm{Tb} + \mathrm{v_e}$$
$$^{150}_{65}\mathrm{Tb} \xrightarrow{\beta^+ \ or \ \text{e.c.}} {}^{150}_{64}\mathrm{Gd} + \mathrm{v_e}$$

From $^{150}_{64}\mathrm{Gd}$ (64 protons, 86 neutrons), alpha decays (yellow boxes) would happen until we reach the stable $^{142}_{60}\mathrm{Nd}$ nuclide.

$$^{150}_{64}\mathrm{Gd} \rightarrow {}^{146}_{62}\mathrm{Sm} + {}^{4}_{2}\mathrm{He}$$
$$^{146}_{62}\mathrm{Sm} \rightarrow {}^{142}_{60}\mathrm{Nd} + {}^{4}_{2}\mathrm{He}$$

The decay series of lutetium–151 (shown in **Figure 5**) is

$$^{151}_{71}\mathrm{Lu} \overset{\mathrm{p}^+}{\rightarrow} {}^{150}_{70}\mathrm{Yb} \overset{?}{\rightarrow} {}^{150}_{69}\mathrm{Tm} \overset{?}{\rightarrow} {}^{150}_{68}\mathrm{Er} \overset{?}{\rightarrow} {}^{150}_{67}\mathrm{Ho} \overset{?}{\rightarrow}$$
$$^{150}_{66}\mathrm{Dy} \overset{?}{\rightarrow} {}^{150}_{65}\mathrm{Tb} \overset{?}{\rightarrow} {}^{150}_{64}\mathrm{Gd} \overset{\alpha}{\rightarrow} {}^{146}_{62}\mathrm{Sm} \overset{\alpha}{\rightarrow} {}^{142}_{60}\mathrm{Nd}$$

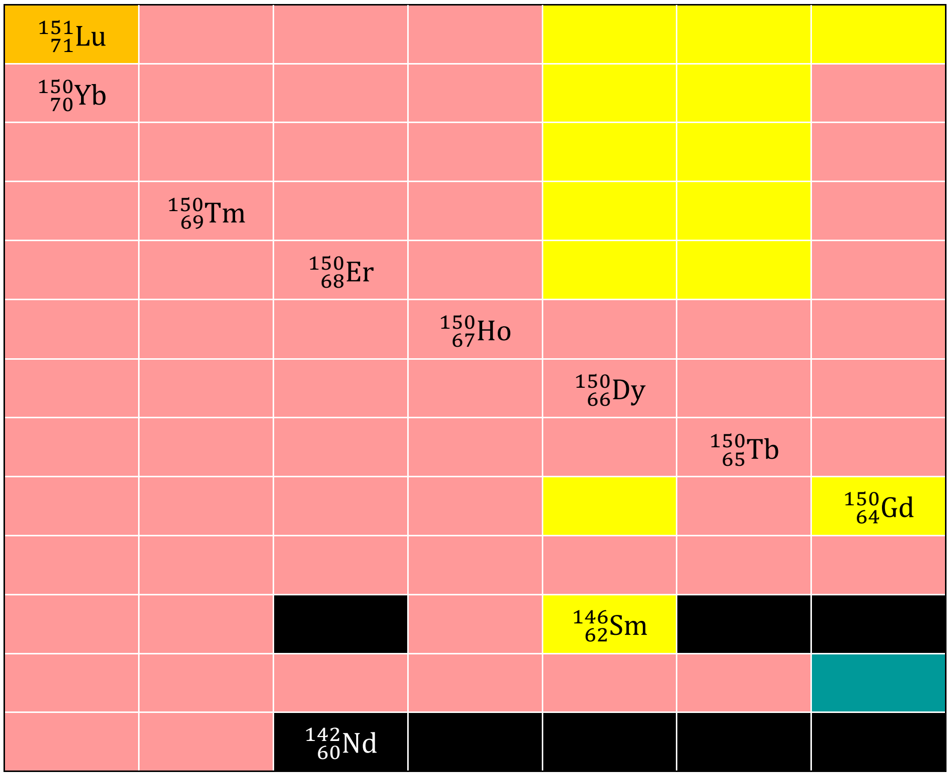


Figure 11 Nuclide Chart Diagram of the decay series of lutetium–151.

How do we know when an electron capture, or a positron emission would happen? A good thing to remember is that *electron capture would be favored mostly in heavier neutron – deficient elements*. This is because it would have a smaller change in mass if electron capture happens as compared to a positron emission.

If the mass of the reacting nuclide is greater than the sum of the mass of the product nuclide and the mass of two electrons, most likely that positron emission would take place.

Sample Problem 8

Predict the type of reaction of the six decays in the previous problem, whether they are positron emissions or electron captures.

Isotope	Atomic Mass (u)
$^{150}_{70}\mathrm{Yb}$	149.95820
$^{150}_{69}\mathrm{Tm}$	149.94996
$^{150}_{68}\mathrm{Er}$	149.93791
$^{150}_{67}\mathrm{Ho}$	149.93350
$^{150}_{66}\mathrm{Dy}$	149.92559
$^{150}_{65}\mathrm{Tb}$	149.92366
$^{150}_{64}\mathrm{Gd}$	149.91866

- To solve this, we would need to compare the mass of the reactant nuclide to the mass of the product nuclide plus two electrons. Knowing that the mass of electrons in kg, we convert it to u.

$$9.1094 \times 10^{-31}\ \mathrm{kg} \times \frac{1\ \mathrm{u}}{1.66054 \times 10^{-27}\ \mathrm{kg}} = 0.00054858\ \mathrm{u}$$

Two electrons would then have a mass of

$$2 \times 0.00054858\ \mathrm{u} = 0.00109716\ \mathrm{u} \approx 0.00110\ \mathrm{u}.$$

We then add the mass of the two electrons to the product nuclides:

Reactant Nuclide	Atomic Mass (u)	Product Nuclide	Atomic Mass (u)	Mass + 2e (u)
$^{150}_{70}\mathrm{Yb}$	149.95820	$^{150}_{69}\mathrm{Tm}$	149.94996	149.95106
$^{150}_{69}\mathrm{Tm}$	149.94996	$^{150}_{68}\mathrm{Er}$	149.93791	149.93901
$^{150}_{68}\mathrm{Er}$	149.93791	$^{150}_{67}\mathrm{Ho}$	149.93350	149.93460
$^{150}_{67}\mathrm{Ho}$	149.93350	$^{150}_{66}\mathrm{Dy}$	149.92559	149.92669
$^{150}_{66}\mathrm{Dy}$	149.92559	$^{150}_{65}\mathrm{Tb}$	149.92366	149.92476
$^{150}_{65}\mathrm{Tb}$	149.92366	$^{150}_{64}\mathrm{Gd}$	149.91866	149.91976

Sample Problem 8 cont.

All the masses of the reactant nuclides are larger than the masses of the product nuclides plus two electrons. This would mean that all of them are positron emission reactions. Updating the decay series of lutetium–151, we have

$$ {}^{151}_{71}\mathrm{Lu} \xrightarrow{\mathrm{p}^+} {}^{150}_{70}\mathrm{Yb} \xrightarrow{\beta^+} {}^{150}_{69}\mathrm{Tm} \xrightarrow{\beta^+} {}^{150}_{68}\mathrm{Er} \xrightarrow{\beta^+} {}^{150}_{67}\mathrm{Ho} \xrightarrow{\beta^+} $$

$$ {}^{150}_{66}\mathrm{Dy} \xrightarrow{\beta^+} {}^{150}_{65}\mathrm{Tb} \xrightarrow{\beta^+} {}^{150}_{64}\mathrm{Gd} \xrightarrow{\alpha} {}^{146}_{62}\mathrm{Sm} \xrightarrow{\alpha} {}^{142}_{60}\mathrm{Nd} $$

This procedure would also show that magnesium–23 would undergo positron emission. (You could try to solve for that, with the isotopic mass of magnesium–23 as $22.99412\ \mathrm{u}$, and sodium – 23 has an isotopic mass of $22.98977\ \mathrm{u}$.)

Additional Information

Never confuse unstable as fast reacting. An unstable nuclide could have a half – life shorter than a second, while others could take years, or even several millennia before reaching their half – life. These ones that have relatively high longevity are referred to as **metastable**.

As an example, the isotope tantalum – 180m (the m here stands for metastable) is an excited state nuclide but has a calculated half – life of at least 4.5×10^{16} years, which is about three million times the current age of the universe.

Activities and Assessments:

Using the interactive nuclide chart, predict the most probable decay series of the following [take note of the differences in color coding]; silicon–43, xenon–110, and protactinium–230.

LESSON 7: NUCLEAR CHEMISTRY
UNIT 5: The Mass-Energy Equivalence

Introduction:

So how does a nuclear reaction release so much energy? We turn to one of the most famous scientists of the twentieth century to find out: Albert Einstein, and his mass – energy equivalence.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Define nuclear binding energy and mass defect.
2. Apply the mass – energy equivalence equation to calculate energies contained in nuclear reactions.

Course Materials:

The term “nuclear” is associated nowadays to a strong energy event, whether it is about the energy sources of a nuclear power plant, or from the catastrophe that the atomic bombs did in Hiroshima and Nagasaki at the tail end of World War II. Where do we get this energy?

We attribute the source of this energy from the **nuclear binding energy**. This energy is the smallest amount of energy required to break down a nucleus of an atom into its elementary particles. Having a higher nuclear binding energy means that the nucleus is more stable.

For a more accurate description of the stability of nuclides, we divide the nuclear binding energy by the number of nucleons (total number of protons and neutrons, or simply mass number) to obtain the **binding energy per nucleon** or BEN:

$$\mathrm{BEN} = \frac{\mathrm{E_b}}{\mathrm{A}}$$

in which $\mathrm{E_b}$ is the nuclear binding energy, and A is the mass number.

The graph of BEN for stable nuclei as a function of A is shown on **Figure 6**.

To obtain the binding energy, we need to know the source of this energy. Via careful experimentation, it is shown that when you add all the individual masses of the protons, neutrons, and electrons of an atom, it will be larger than the mass of the atom itself. This difference is termed as the **mass defect**.

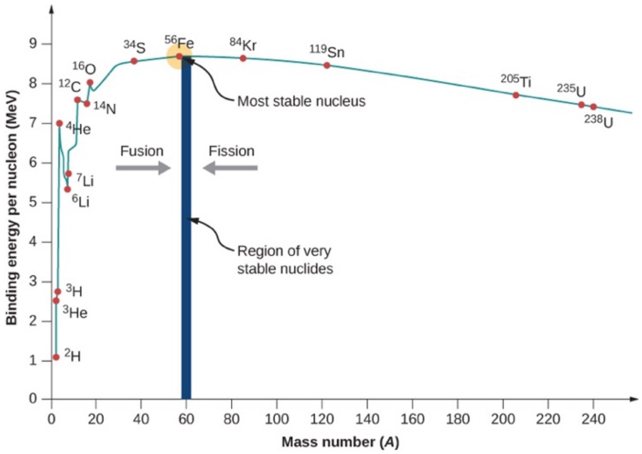


Figure 12 *Graph of binding energy per nucleon of stable nuclei. Iron–56 is the most stable nucleus, as shown in this graph. Being the most stable nucleus, smaller nuclei does fusion, while larger nuclei does fission so that they can achieve the same stability or be near it. Both processes are exothermic in nature. Obtained from https://phys.libretexts.org/Bookshelves/University_Physics/Book%3A_University_Physics_(OpenStax) under a Creative Commons Attribution License (by 4.0).*

So, how do we relate mass defect and nuclear binding energy? This was answered by one of the most famous equations of Einstein: the **mass – energy equivalence**, or simply:

$$\mathrm{E} = \mathrm{mc}^2$$

This equation relates the mass defect $(\Delta\mathrm{m})$ and the nuclear binding energy $(\mathrm{E_b})$, having the square of the speed of light in a vacuum as the direct proportionality constant:

$$\mathrm{E_b} = (\Delta\mathrm{m})\mathrm{c}^2$$

Sample Problem 9

Tritium, ${}^{3}_{1}\mathrm{H}$, is the radioactive isotope of hydrogen. It has an isotopic mass of $3.0160492\ \mathrm{u}$. What is the binding energy of a tritium atom? What is the binding energy of a mole of tritium atoms?

- First, we need to convert u to kg:

$$3.0160492\ \mathrm{u} \times \frac{1.66054 \times 10^{-27}\ \mathrm{kg}}{1\ \mathrm{u}} = 5.00827 \times 10^{-27}\ \mathrm{kg}$$

Calculating the sum of the individual masses of the nucleons in tritium (one proton and two neutrons)

$$1.6726 \times 10^{-27}\ \mathrm{kg} + 2(1.6749 \times 10^{-27}\ \mathrm{kg}) = 5.0224\ \times 10^{-27}\ \mathrm{kg}$$

Sample Problem 9 cont.

The mass defect is:

$$\Delta\mathrm{m} = 5.0224\ \times 10^{-27}\ \mathrm{kg} - 5.00827 \times 10^{-27}\ \mathrm{kg} = 1.413 \times 10^{-29}\ \mathrm{kg}$$

Solving for the nuclear binding energy:

$$\mathrm{E_b} = (\Delta\mathrm{m})\mathrm{c}^2$$

$$\mathrm{E_b} = (1.413 \times 10^{-29}\ \mathrm{kg})\left(2.998 \times 10^{8}\,\frac{\mathrm{m}}{\mathrm{s}}\right)^2 = 1.27 \times 10^{-12}\ \mathrm{J}$$

The value is small, so we usually convert this into megaelectron volts (MeV).

$$\mathrm{E_b} = 1.27 \times 10^{-12}\ \mathrm{J} \times \frac{1\ \mathrm{MeV}}{1.60 \times 10^{-13}\ \mathrm{J}} = 7.94\ \mathrm{MeV}$$

- For a mole of tritium atoms:

$$\mathrm{E_b} = 1.27 \times 10^{-12}\ \mathrm{J} \times 6.022 \times 10^{23}\ \mathrm{mol}^{-1} = 7.65 \times 10^{11}\,\frac{\mathrm{J}}{\mathrm{mol}}$$

Activities and Assessments:

Calculate the nuclear binding energy for a helium–5 atom (isotopic mass = 5.012057 u), a sodium–22 atom (isotopic mass = 21.99443742 u), and a cobalt–60 atom (isotopic mass = 59.9338222 u).

LESSON 7: NUCLEAR CHEMISTRY
UNIT 6: Nuclear Transmutation

Introduction:

We now discuss nuclear reactions that are not necessarily naturally occurring, and usually requires an input of energy to start. Nuclear transmutations are thought of as the modern alchemy procedures that the scientists of old have no ability to do so.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Describe a nuclear transmutation.
2. Apply the shorthand notation on describing a nuclear transmutation.
3. Predict missing components of a nuclear transmutation.

Course Materials:

Nuclear transmutation is defined as the transformation of one nuclide into another, via bombardment of particles. It is essentially the opposite of a nuclear decay. As such, these reactions are nonspontaneous.

There are nuclear transmutations that are naturally occurring in our environment. One such reaction is the production of carbon–14 in the atmosphere. It is formed by the absorption of neutrons (from cosmic rays in the upper atmospheres) by the nitrogen–14 atoms.

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \rightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{p}$$

We classify transmutations based on what particle is used to bombard the nuclide (as it usually requires high energy) and what particle is released by the nucleus after bombardment. For the neutron bombardment of nitrogen–14, we call them as an (n,p) reaction since the neutron is absorbed by the nucleus, and a proton is released by the nucleus. This type of reactions can be written in a shorthand notation: writing, in order, the reacting nuclide, the bombarding particle, the ejected particle and the product nuclide. We enclose the particles inside parentheses. For the previous reaction, the shorthand is

$$^{14}_{7}\mathrm{N}\ (\mathrm{n}, \mathrm{p})\ ^{14}_{6}\mathrm{C}$$

Remember that to balance these equations, the total Z and A should be equal in both sides.

Sample Problem 10

Write the shorthand notations of the following nuclear transmutations:

- $^{129}_{53}\mathrm{I} + ^{1}_{0}\mathrm{n} \rightarrow ^{130}_{54}\mathrm{Xe} + ^{0}_{-1}\beta$
- $^{239}_{94}\mathrm{Pu} + ^{4}_{2}\mathrm{He} \rightarrow ^{242}_{96}\mathrm{Cm} + ^{1}_{0}\mathrm{n}$
- $^{10}_{5}\mathrm{B} + ^{1}_{0}\mathrm{n} \rightarrow ^{7}_{3}\mathrm{Li} + ^{4}_{2}\mathrm{He}$

- For the first reaction, we have a neutron as the absorbed particle, and a beta particle as the ejected particle. Thus, the shorthand would be

$$^{129}_{53}\mathrm{I}\ (\mathrm{n}, \beta^{-})\ ^{130}_{54}\mathrm{Xe}$$

- For the second reaction, we have an alpha particle as the absorbed particle, and a neutron as the ejected particle. Thus, the shorthand would be

$$^{239}_{94}\mathrm{Pu}\ (\alpha, \mathrm{n})\ ^{242}_{96}\mathrm{Cm}$$

- For the third reaction, we have a neutron as the absorbed particle, and an alpha particle as the ejected particle. Thus, the shorthand would be

$$^{10}_{5}\mathrm{B}\ (\mathrm{n}, \alpha)\ ^{7}_{3}\mathrm{Li}$$

Note: the first nuclear reaction shown in unit 1 is a nuclear transmutation, while the second one is an electron capture reaction. Following our shorthand notation, we would have

$$^{196}_{80}\mathrm{Hg}\ (\mathrm{n}, \gamma)\ ^{197}_{80}\mathrm{Hg}$$

Sample Problem 11

Predict the missing nuclide / particle and write the complete reactions of the following shorthand nuclear transmutations:

- $^{16}_{8}\mathrm{O}\ (\mathrm{p}, \alpha)\ ?$
- $^{27}_{13}\mathrm{Al}\ (?, \alpha)\ ^{24}_{11}\mathrm{Na}$
- $^{13}_{6}\mathrm{C}\ (\mathrm{n}, ?)\ ^{14}_{6}\mathrm{C}$
- $?\ (\alpha, \mathrm{p})\ ^{17}_{8}\mathrm{O}$

- We write the first reaction as

$$^{16}_{8}\mathrm{O} + ^{1}_{1}\mathrm{p} \rightarrow ? + ^{4}_{2}\mathrm{He}$$

To balance this, we determine the totals of both sides: The left side has $\mathrm{Z_L} = 8 + 1 = 9$, and $\mathrm{A_L} = 16 + 1 = 17$. The right side has $\mathrm{Z_R} = \mathrm{Z} + 2$, and $\mathrm{A_R} = \mathrm{A} + 4$. Since $\mathrm{Z_L} = \mathrm{Z_R}$ and $\mathrm{A_L} = \mathrm{A_R}$, $\mathrm{Z} = 9 - 2 = 7$ and $\mathrm{A} = 17 - 4 = 13$. The element with seven as its atomic number is nitrogen, so the missing nuclide is nitrogen–13. Therefore, the reaction is

$$^{16}_{8}\mathrm{O} + ^{1}_{1}\mathrm{p} \rightarrow ^{13}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He}$$

- We write the second reaction as

$$^{27}_{13}\mathrm{Al} + ? \rightarrow ^{24}_{11}\mathrm{Na} + ^{4}_{2}\mathrm{He}$$

To balance this, we determine the totals of both sides: The left side has $\mathrm{Z_L} = 13 + \mathrm{Z}$, and $\mathrm{A_L} = 27 + \mathrm{A}$. The right side has $\mathrm{Z_R} = 11 + 2 = 13$, and $\mathrm{A_R} = 24 + 4 = 28$. Since $\mathrm{Z_L} = \mathrm{Z_R}$ and $\mathrm{A_L} = \mathrm{A_R}$, $\mathrm{Z} = 13 - 13 = 0$ and $\mathrm{A} = 28 - 27 = 1$. A neutron is described by having a zero atomic number and one as its mass

Sample Problem 11 cont.

number. We then write the reaction as

$$^{27}_{13}\mathrm{Al} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{24}_{11}\mathrm{Na} + {}^{4}_{2}\mathrm{He}$$

- We write the third reaction as

  $$^{13}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + ?$$

  Notice that the identity of the element did not change. This means that the atomic number did not change. We can also see that the mass number of the product nuclide is equal to the sum of the mass numbers of the reactant side. This means that the missing nuclide has $\mathrm{Z} = 0$ and $\mathrm{A} = 0$. This pertains to a gamma ray. The reaction, therefore, is

  $$^{13}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{0}_{0}\gamma$$

  We again attribute the release of the gamma ray as a way for the excited nuclide to relax, and release energy.

- We write the fourth reaction as

  $$? + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p}$$

  To balance this, we determine the totals of both sides: The left side has $\mathrm{Z_L} = \mathrm{Z} + 2$, and $\mathrm{A_L} = \mathrm{A} + 4$. The right side has $\mathrm{Z_R} = 8 + 1 = 9$, and $\mathrm{A_R} = 17 + 1 = 18$. Since $\mathrm{Z_L} = \mathrm{Z_R}$ and $\mathrm{A_L} = \mathrm{A_R}$, $\mathrm{Z} = 9 - 2 = 7$ and $\mathrm{A} = 17 - 4 = 13$. Nitrogen has an atomic number of seven. Therefore, the reaction would be written as

  $$^{13}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p}$$

  This reaction is generally known as the first induced nuclear transmutation, credited to Ernest Rutherford in 1919 about his experiments conducted in the University of Manchester. This also led to the discovery of the proton as a subatomic particle. It is not a surprise that Rutherford is known nowadays as the father of nuclear physics.

Activities and Assessments:

Complete the following shorthand notations:

- $? \ (\mathrm{p}, \alpha) \ {}^{6}_{3}\mathrm{Li}$
- $^{31}_{15}\mathrm{P} \ (\alpha, ?) \ {}^{34}_{16}\mathrm{S}$
- $^{242}_{96}\mathrm{Cm} \ (\alpha, \mathrm{n}) \ ?$
- $^{25}_{12}\mathrm{Mg} \ (?, \mathrm{p}) \ {}^{24}_{11}\mathrm{Na}$

LESSON 7: NUCLEAR CHEMISTRY
UNIT 7: Nuclear Fission and Fusion

Introduction:

The types of reactions that are thought of as the ones with the most energy output are fission and fusion type reactions. These reactions, therefore, are very important, especially their applications to society in both beneficial and harmful ways.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Describe a nuclear fission reaction and a nuclear fusion reaction.
2. Apply the mass – energy equivalence to demonstrate the energy release of these reactions.

Course Materials:

Nuclear fission is a nuclear reaction in which a nuclide, usually large, is split into smaller nuclides and particles, via decay or bombardment of particles. It also releases energy, and the total mass of the products is less than the total mass of the reactants (as stated by the mass – energy equivalence.

Some nuclides naturally decay via fission, as shown in the nuclide chart. These nuclides are especially large and heavy nuclei. We term these decays as **spontaneous fission**. Some other nuclei are capable of spontaneous fission, but it is not the necessarily the kinetically favored reaction. Take for example, plutonium–244 can have spontaneous fission with a variety of released product nuclides and particles, however 99.88% of the time, it will have an alpha decay, as compared to 0.12% of it having spontaneous fission.

Induced fission reactions are fission reactions that require a high energy to conduct. This energy can be via bombardment of a variety of particles or electromagnetic radiation via gamma rays, causing the nuclide to be excited and undergo the fission process.

Commonly, neutrons are by-products of a fission reaction, along with the release of high amounts of energy (from the change in mass, and application of the mass – energy equivalence) and product nuclides. These neutrons, however, could start a new set of fission reactions, especially when there is a good amount of available nuclides. We term this continuous process as a **nuclear chain reaction**. The principle of these chain reactions are used in both nuclear power reactors (controlled, safe) and in nuclear weapons (uncontrolled, dangerous).

To calculate the energy released in a nuclear reaction, we still need to obtain the change in mass. In this case however, this change in mass is between the total mass of the reactants and the total mass of the products.

Sample Problem 12

The spontaneous fission of californium–252 releases xenon–140 and ruthenium–108. How many neutrons are released in this process?

- Writing the following reaction, we have

  $$^{252}_{98}\mathrm{Cf} \rightarrow \; ^{140}_{54}\mathrm{Xe} + \; ^{108}_{44}\mathrm{Ru} + ?\,^{1}_{0}\mathrm{n}$$

  Adding the atomic numbers, we could see that the totals are balanced. For the mass numbers

  $$252 = 140 + 108 + (\mathrm{x})(1)$$

  in which x is the number of neutrons. Solving for x

  $$252 = 248 + \mathrm{x} \Longrightarrow \mathrm{x} = 252 - 248 = 4$$

  Therefore, there are four neutrons that are products of the reaction. The balanced reaction is

  $$^{252}_{98}\mathrm{Cf} \rightarrow \; ^{140}_{54}\mathrm{Xe} + \; ^{108}_{44}\mathrm{Ru} \; + 4\,^{1}_{0}\mathrm{n}$$

Sample Problem 13

The induced fission of uranium–235 releases krypton–92 and barium–141. How many neutrons are released in this process? How much energy does a mole of uranium–235 would release via fission? Compare this to the natural alpha decay of uranium–235.

- Writing the following reaction, we have

  $$^{235}_{92}\mathrm{U} \; + \,^{1}_{0}\mathrm{n} \rightarrow \; ^{92}_{36}\mathrm{Kr} + \; ^{141}_{56}\mathrm{Ba} \; + ?\,^{1}_{0}\mathrm{n}$$

  Adding the atomic numbers, we could see that the totals are balanced. For the mass numbers

  $$235 + 1 = 92 + 141 + (\mathrm{x})(1)$$

  in which x is the number of neutrons. Solving for x

  $$236 = 233 + \mathrm{x} \Longrightarrow \mathrm{x} = 236 - 233 = 3$$

  Therefore, there are three neutrons that are products of the reaction. The balanced reaction is

  $$^{235}_{92}\mathrm{U} \; + \,^{1}_{0}\mathrm{n} \rightarrow \; ^{92}_{36}\mathrm{Kr} + \; ^{141}_{56}\mathrm{Ba} \; + 3\,^{1}_{0}\mathrm{n}$$

Sample Problem 13 cont.

- The isotope masses are shown below:

Isotope	Atomic Mass (u)
${}^{235}_{92}\mathrm{U}$	235.0439299
${}^{92}_{36}\mathrm{Kr}$	91.926156
${}^{141}_{56}\mathrm{Ba}$	140.914412
${}^{231}_{90}\mathrm{Th}$	231.036304
${}^{4}_{2}\mathrm{He}$	4.001506

A neutron would have a mass of

$$1.6749 \times 10^{-27}\ \mathrm{kg} \times \frac{1\ \mathrm{u}}{1.66054 \times 10^{-27}\ \mathrm{kg}} = 1.0086478\ \mathrm{u}$$

For the change in mass of uranium – 235 fission, the total mass of the reactants is

$$235.0439299\ \mathrm{u} + 1.0086478\ \mathrm{u} = 236.0525777\ \mathrm{u}$$

The total mass of the products is

$$91.926156\ \mathrm{u} + 140.914412\ \mathrm{u} + 3(1.0086478\ \mathrm{u}) = 235.8665114\ \mathrm{u}$$

The change in mass is

$$236.0525777\ \mathrm{u} - 235.8665114\ \mathrm{u} = 0.1860663\ \mathrm{u}$$

Converting this to kg:

$$0.1860663\ \mathrm{u} \times \frac{1.66054 \times 10^{-27}\ \mathrm{kg}}{1\ \mathrm{u}} = 3.089705 \times 10^{-28}\ \mathrm{kg}$$

Using the mass – energy equivalence

$$\mathrm{E} = (\Delta \mathrm{m})\mathrm{c}^2$$

$$\mathrm{E} = (3.089705 \times 10^{-28}\ \mathrm{kg})\left(2.998 \times 10^{8}\ \frac{\mathrm{m}}{\mathrm{s}}\right)^2 = 2.777028 \times 10^{-11}\ \mathrm{J}$$

For one mole of uranium–235,

$$2.777028 \times 10^{-11}\ \mathrm{J} \times 6.022 \times 10^{23}\ \mathrm{mol}^{-1} = 1.672326 \times 10^{13}\ \frac{\mathrm{J}}{\mathrm{mol}}$$

- The alpha decay of uranium–235 is

$${}^{235}_{92}\mathrm{U} \rightarrow {}^{231}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

The change in mass is

$$235.0439299\ \mathrm{u} - (231.036304\ \mathrm{u} + 4.001506\ \mathrm{u}) = 0.0061199\ \mathrm{u}$$

$$0.0061199\ \mathrm{u} \times \frac{1.66054 \times 10^{-27}\ \mathrm{kg}}{1\ \mathrm{u}} = 1.016234 \times 10^{-29}\ \mathrm{kg}$$

The energy released would be

$$\mathrm{E} = (1.016234 \times 10^{-29}\ \mathrm{kg})\left(2.998 \times 10^{8}\ \frac{\mathrm{m}}{\mathrm{s}}\right)^2 = 9.133915 \times 10^{-13}\ \mathrm{J}$$

For one mole of uranium–235,

$$9.133915 \times 10^{-13}\ \mathrm{J} \times 6.022 \times 10^{23}\ \mathrm{mol}^{-1} = 5.500444 \times 10^{11}\ \frac{\mathrm{J}}{\mathrm{mol}}$$

Sample Problem 13 cont.

Notice that the uranium fission has a higher energy as compared to the alpha decay of uranium by around thirty times. It is also important to know that just by investing one neutron in the nuclear fission, three neutrons would be produced, which in turn would initiate new nuclear fissions of uranium–235 (provided that they are available in the reaction system). Alpha decay of uranium–235 has a half – life of around 700 million years, so to wait for one mole of uranium–235 would most likely be longer (and the energy would be distributed on that time span) as compared to a fission setup where the reaction would sustain itself (termed as a critical condition, with the correct amount as the critical mass).

Do note that the Little Boy atomic bomb dropped in Hiroshima has this reaction in concept.

Nuclear fusion happens when light nuclides are forced together, causing them to combine into one or more nuclides and additional particles. Similar with fission, the total mass of the products will be less than the total mass of the reactants, as the reaction also releases energy (as stated by the mass – energy equivalence).

Important fusion reactions are still in the sun, as well as all stars in the universe. The origin of virtually all elements is attributed to these stars, which we call the process as **nucleosynthesis**.

Sample Problem 14

One of the important synthesis reaction cycles to produce helium in stars is called the Bethe–Weizsäcker cycle, or the CNO-I cycle. From carbon–12, the step – by – step processes are a hydrogen fusion, a positron emission, two hydrogen fusions, a positron emission, and a hydrogen fusion with a released alpha particle. Determine the nuclear reactions.

- Starting with carbon–12, it is given that

$$^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \rightarrow ?$$

Since there are no side products, we just add both the atomic number and mass number. We then have $\mathrm{Z} = 7$ and $\mathrm{A} = 13$. This pertains to nitrogen–13, so

$$^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \rightarrow ^{13}_{7}\mathrm{N}$$

- For the positron emission of nitrogen–13,

$$^{13}_{7}\mathrm{N} \rightarrow ? + ^{0}_{1}\beta + \mathrm{v_e}$$

Having a constant mass number, and subtracting one to the atomic number, we know that carbon–13 is produced, so

$$^{13}_{7}\mathrm{N} \rightarrow ^{13}_{6}\mathrm{C} + ^{0}_{1}\beta + \mathrm{v_e}$$

Sample Problem 14 cont.

- With carbon–13 and its hydrogen fusion,

  $${}^{13}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \rightarrow ?$$

  Since there are no side products, we just add both the atomic number and mass number. We then have $\mathrm{Z} = 7$ and $\mathrm{A} = 14$. This pertains to nitrogen–14, so

  $${}^{13}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{14}_{7}\mathrm{N}$$

- The hydrogen fusion of nitrogen–14 is

  $${}^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow ?$$

  Since there are no side products, we just add both the atomic number and mass number. We then have $\mathrm{Z} = 8$ and $\mathrm{A} = 15$. This pertains to oxygen–15, so

  $${}^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{15}_{8}\mathrm{O}$$

- For the positron emission of oxygen–15,

  $${}^{15}_{8}\mathrm{O} \rightarrow ? + {}^{0}_{1}\beta + \mathrm{v_e}$$

  Having a constant mass number, and subtracting one to the atomic number, we know that nitrogen–15 is produced, so

  $${}^{15}_{8}\mathrm{O} \rightarrow {}^{15}_{7}\mathrm{N} + {}^{0}_{1}\beta + \mathrm{v_e}$$

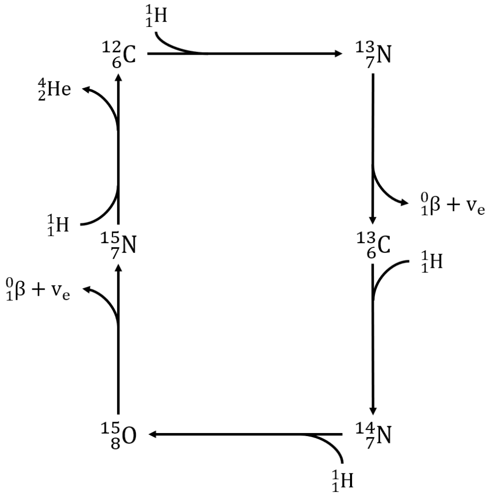
- For the final reaction, it is given that

  $${}^{15}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow ? + {}^{4}_{2}\mathrm{He}$$

  Computing for the missing nuclide, we have $\mathrm{Z} = 7 + 1 - 2 = 6$ and $\mathrm{A} = 15 + 1 - 4 = 12$. Therefore, the missing nuclide is carbon–12, thus completing the cycle. The reaction is

  $${}^{15}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{4}_{2}\mathrm{He}$$

  The overall cycle is



Most scientists believe that fusion reactors are the next step in nuclear power technology. They determined that these reactors can be fueled by deuterium and tritium, both isotopes of hydrogen. Deuterium is available in various sources of water, and so it is evaluated that the Earth has a bountiful supply of it as long as there is water in Earth. The problem is that so far it is not feasible, because of a lot of parameters that have not been met. We hope for a future where this type of technology would be achievable.

Activities and Assessments:

1. Calculate the energy released by the reaction given in sample problem 12 and compare it to the energy released by the alpha decay of californium–252.

$$^{252}_{98}\mathrm{Cf} \rightarrow \; ^{140}_{54}\mathrm{Xe} + \; ^{108}_{44}\mathrm{Ru} \; + 4\; ^{1}_{0}\mathrm{n}$$
$$^{252}_{98}\mathrm{Cf} \rightarrow \; ^{248}_{96}\mathrm{Cm} + \; ^{4}_{2}\mathrm{He}$$

Isotope	Atomic Mass (u)
$^{252}_{98}\mathrm{Cf}$	252.081626
$^{140}_{54}\mathrm{Xe}$	139.92165
$^{108}_{44}\mathrm{Ru}$	107.91017
$^{248}_{96}\mathrm{Cm}$	248.072349
$^{4}_{2}\mathrm{He}$	4.001506

2. The CNO-IV cycle is a related cycle to the CNO-I cycle but is only seen on massive stars. It starts with an oxygen–18 nuclide and conducts the following steps: a hydrogen fusion with a gamma ray release, a hydrogen fusion with a release of an alpha particle, a hydrogen fusion with a gamma ray release, a positron emission, a hydrogen fusion with a gamma ray release, and a positron emission. Determine the nuclear reactions and draw a cycle that represents the CNO-IV cycle.

LESSON 7: NUCLEAR CHEMISTRY
UNIT 8: Nuclear Radiation

Introduction:

Radiation has a bad reputation, as it is usually a related term to mutation, cancer and other terms that are not necessarily a good thing. We need to correct those statements so that we could correctly describe these radiations.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Describe the properties of radiation.
2. Compare the penetration capabilities of ionizing radiation.

Course Materials:

Almost all nuclear reactions deal with nuclear radiation. We can classify these radiations based on what they give off as products. **Alpha radiation** happens when alpha particles are released, **beta radiation** when beta particles are a product, and **gamma radiation** when gamma rays are released. Fast neutrons could also be accounted for radiation but is seldom found outside nuclear fission reactors.

We could classify radiation as a **particle radiation**, in which a particle is given off (alpha particles, beta particles and neutrons), or an **electromagnetic radiation**, in which only pure energy is radiated, without any mass whatsoever (gamma rays). **X-rays** are also classified as electromagnetic radiation. They are very identical to gamma rays, but they usually have a non-nuclear origin. We include x-rays in our discussion of radiation as a reference.

Additional Information

X-rays are produced by electrons, protons, or ions, with enough energy, that hit a material that acts as the opposite electrode of the particle used. Medical x-ray tubes usually use tungsten as the material target.

Another classification of radiation is if it affects matter that it hits or passes through. **Non-ionizing radiation** would not have enough energy to break molecular bonding or remove an electron from an atom. This is the typical radiations that we encounter; visible light, heat, radio waves and microwaves are all examples of this radiation.

Ionizing radiation, however, has enough energy for bond breaking or electron removing. All the particle radiations mentioned, as well as both gamma rays and x-rays are ionizing in nature.
The ionizing radiations have differing penetration capabilities.

- Alpha particles are the least penetrating, as it can be easily blocked by paper, or even the air.
- Beta particles can pass through paper, and the human skin, but is blocked by thin sheets of metal or plastic, or a thick piece of wood.

- Both gamma rays and x-rays have higher penetration capabilities, and require a very thick layer of concrete, or a thick layer of dense materials, like lead.
- Fast neutrons have exceptional penetrating power, requiring very thick layers of concrete or water, which should also contain hydrogen, to neutralize their penetration capabilities.

The penetration capabilities of these radiations are shown in **Figure 13**.
This does not mean that it is always dangerous to be in the presence of ionizing radiation. Some of these are beneficial in various applications, which we would discuss later.
As said before, becquerel and curie are units of the amount of radiation. They pertain to the radiation emitted by a source. As we know, not all that radiation would reach a target. This means that we need another measurement for radiation exposure dose, or the amount of radiation absorbed, as applied to human beings.
We define a **sievert** (Sv) as the amount of radiation energy absorbed in a human's body per unit mass $(\mathrm{J/kg})$. A comparison of absorbed doses is shown in https://xkcd.com/radiation/.

Additional Information

Some people use the banana equivalent dose (BED) as a more accessible unit for comparison of radiation exposure dose. It is equivalent to $0.1\ \mu\mathrm{Sv}$, and is estimated as the amount of radiation that the body absorbs after eating one banana.
How is a banana radioactive? It is because they naturally contain potassium–40, which is radioactive. Do not be scared though, as this dose is very small. In fact, you need to eat around 200 bananas to have an equivalent amount of radiation in a chest x-ray, a chest CT scan would be equivalent to 70,000 bananas, and a sure fatal dose would be 80,000,000 bananas!
Another important thing to consider is that the body has natural regulation reactions when it comes to potassium–40 (as the body can expel the radioactive isotope), so overall, its amount inside the body is constant. Eat as much bananas as you like!

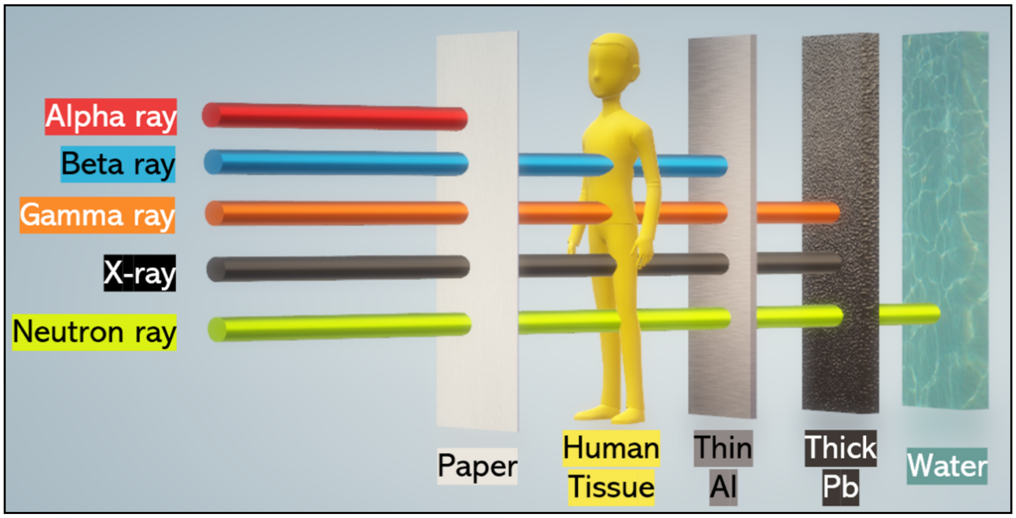


Figure 7 Degrees of Penetration of the Ionizing Radiation

Activities and Assessments:

How would you then design a house that can shield you from nuclear radiation in case there is nuclear fallout in your vicinity? Would it be practical to do so?

LESSON 7: NUCLEAR CHEMISTRY
UNIT 9: Applications of Nuclear Reactions

Introduction:

How do we now use the knowledge surrounding these nuclear reactions? It turns out that a lot of convenient and important applications are, in principle, guided by the nuclear reactions that we have studied so far. Let us look at some of them.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Describe types pf nuclear accidents by their scope.
2. Discuss various applications of nuclear reactions in medicine, food, and other industries.

Course Materials:

Nuclear reactions have already been utilized by various industries in the world. Most of its controlled applications are beneficial, but again that control should be strictly implemented. Let us discuss these applications.

Nuclear reactors are facilities that utilize controlled nuclear reactions (mostly nuclear fissions) as a source of energy. They usually utilize uranium–235 as the primary source in the core. The reaction is controlled in a way that the chain reaction would proceed, but the number of neutrons produced is observed and adjusted accordingly. Too few of the yielded neutrons and the chain reaction would stop. Too many neutrons would make the reaction uncontrolled and will most likely result in damage and destruction via an explosion and / or what we call as a **nuclear meltdown**, damages caused by overheating of the core.

Nuclear accidents are categorized using the International Nuclear and Radiological Event Scale, or simply **INES**. It is a logarithmic scale (like the Richter magnitude scale for earthquakes) in which a level is usually perceived as ten times the intensity of a previous level. So far, there are eight levels, from zero to seven.

- An event that has no safety relevance is considered as “out of scale”. One such example is an unknown parcel, which is thought of as a bomb, was discovered near a nuclear plant in the U.S. (1999)
- A **0** in the INES is called a deviation, in which no safety significance is registered. A shutdown of a reactor in Argentina because of an increase in tritium in the compartments of the reactor (2006) is an example.
- A **1** in the INES is an anomaly, which include overexposure more than the annual limit (1 mSv for a member of the public), or lower impact problems. An example would be discoveries of cracks in graphite bricks above the limit in a nuclear power station in the U.K. (2018)
- A **2** in the INES is an incident, with higher than 10 mSv exposure to the public or the annual limit of workers (50 mSv), or significant failures in safety but with no actual consequences. A short circuit causing the shutdown of a reactor in Germany because of the weather (1977) is an example.
- A **3** in the INES is a serious incident, in which ten times the worker limit has been reached, or near – accidents and loss of a radioactive source happened. An example would be a fire in a nuclear reactor in Spain caused a shutdown because of the destruction of control systems (1989).

- A **4** in the INES is an accident with local consequences. This include at least one death from radiation, or release of significant amounts of radioactive material that has high probability of public exposure. Leakage of around 770,000 tons of highly radioactive water in the Barents Sea due to a damage in nuclear facility in once known as the Soviet Union (1982) is an example.
- A **5** in the INES is an accident with wider consequences. This include limited release of radioactive material that require planned countermeasures, and several deaths from radiation has occurred. The Goiâna accident in Brazil is classified as this.
- A **6** in the INES is a serious accident, in which a significant release of radioactive material that require planned countermeasures has occurred. Only one of these has been regarded, so far; the Kyshtym disaster of 1957.
- A **7** in the INES is a major accident, in which a major release of radioactive material that require planned countermeasures has occurred. The Chernobyl disaster of 1986, and the Fukushima Daiichi nuclear disaster of 2011 are the only two events that are Level 7 accidents. They are also probably the two most famous nuclear accidents.

Nuclear reactors usually employ **control rods** for the regulation of the neutron flux. They are usually made of boron or cadmium metal, and these absorb the neutrons. Raising or lowering these rods would decrease or increase the neutron flux.

Some of the neutrons are also very energetic and fast, and they are aptly called as **fast neutrons**. Nuclear reactors employ what we call as **moderators** to help lessen the energies of these neutrons. Usually, water or deuterated water is used as a moderator. They also function as **coolants** in this case, since the reactions all produce a lot of heat.

Positron Emission Tomography scans, or more commonly known as **PET scans**, are used to image the physiological aspects of the body rather than the anatomy (as a CT scan would do). It employs using radionuclides that have short half – lives for tracing of its activities in the body, and are positron emissions, since the scanner employs electrons, and this particle – antiparticle pair would produce two gamma rays that are detected in the scan. Most applications would be in clinical diagnosis of certain diseases and disorders, especially the determination of benign or malignant tumors. **Table 2** shows the used nuclides for this type of scanning.

Table 2 Radionuclides used as tracers in PET Scans and their target uses

Nuclide	**Target**
Carbon–11	Brain scan imaging
Nitrogen–13	Brain, heart, and liver scan imaging
Oxygen–15	Lung functions
Fluorine–18	Bone scanning and sugar metabolism in the brain
Copper–64	Diagnosis of lung and liver diseases
Krypton–79	Cardiovascular function assessments

Radiation therapy is the use of high doses of radiation to kill cancer cells and lessen the size of tumors. It could be employed as an external beam radiotherapy (EBRT) where an outside source of irradiation (usually x-rays, but gamma rays from cobalt-60 could also be used) is directed at the tumor from outside the body, an unsealed source radionuclide therapy (RNT) where injection or ingestion of radiopharmaceuticals (medicine using radioactive nuclides like iodine–131 for thyroid conditions, radium–223, strontium–89, and samarium–153 for bone metastasis, phosphorus–32 for bone marrow conditions, and yttrium–90 for liver tumors, among others), or via brachytherapy where a sealed radiation source (usually iodine–125 or cesium–131, inside a protective capsule or wire that allows the radiation to take place without the contents dissolving in the body fluids) is attached near the target tumor.

Food irradiation is the application of ionizing radiation in food. Contrary to some beliefs, it does not make a food radioactive. It also maintains the nutritional quality and the consistency of the food's taste, texture, or appearance.

Food irradiation is employed because it extends the shelf life of food, and it improves the food's safety since it eradicates insects and microorganisms that can grow in the food itself. So far, there have no proved long – term effects of consumption of irradiated food.
Food irradiation usually employs x-rays (non – nuclear origin) or gamma rays (sourced from either cobalt–60 or cesium–137).

Radioactive dating is the employment of comparing abundance ratios of a radioactive isotope to estimate the age of a material. Materials that are from living sources have their age tested using carbon–14 as a basis (called carbon dating). This is because a dead source could not exchange carbon from the environment it has, and so the intact carbon–14 in the sample would undergo its radioactive decay; fewer carbon–14 than the typical ratio of carbon–14 to carbon–12 would mean that the sample has gone into radioactive decay. Using the half-life of carbon–14 as a basis (around 5730 years), we could estimate the age of the sample.
For non – living sources, other radionuclides are employed; uranium – lead dating (using the decay series of uranium–235 to lead–207 and uranium–238 to lead–206) for zircon samples, potassium – argon dating (uses electron capture / positron decay of potassium–40 to argon–40) for micas, feldspars and hornblendes, and the iodine–129 – xenon–129 chronometer for meteorite age dating.
The use of nuclear reactions in warfare is also extensive. Mine detectors employ sensors that detect nitrogen radioactivity, which would differentiate them from just scraps of metal on the ground. The usage of nuclear weapons and the destruction it caused towards the end of World War II, and the Cold War threats from the development of these weapons, caused the signing of the Nuclear Non-Proliferation Treaty, as a way to prevent the transfer of nuclear weapons (non-proliferation), cessation of the nuclear arms race (disarmament), and the development of nuclear energy for peaceful purposes.
Other uses that employ various nuclear reactions include the following: smoke detectors (which contains americium–241 that releases alpha particles in the short range of air, maintaining a circuit that would be obstructed by smoke), neutron activation analysis (usage of bombardment of neutrons to determine concentration of a stable element in a sample, first applied in an iridium sample attributed to an asteroid impact) now used to determine the amount of chemicals inside paintings, and industrial applications like the use of gamma rays to evaluate the thickness of parts in the automobile, aircraft and construction industries.

Activities and Assessments:

You are asked to give an opinion about whether the Bataan Nuclear Power Plant should be reopened or not. Give both advantages and disadvantages of doing so, and by weighing these, state if you are pro or anti in the reopening of the said power plant.

LESSON 8: ELECTROCHEMISTRY
UNIT 1: Fundamentals of Electrochemistry

Introduction:

Chemical reactions involve the transfer of electrons from one atom or molecule to another – a process called the reduction-oxidation (redox) reaction. In this chapter, we will discuss first the fundamentals of electrochemistry: the redox reactions and the notations needed.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Balance redox reactions in acidic or basic media.
2. Identify the two general types of cell: voltaic cells and electrolytic cells.
3. Construct cell notations from chemical equations or cell diagrams.

Course Materials:

Electrochemistry is the branch of chemistry that deal with the interconversion of electrical energy and chemical energy. Electrochemical processes are redox reaction in which the energy released by spontaneous reaction is converted to electricity, or in which electrical energy is used to cause a nonspontaneous reaction to occur. In order to understand this further, we will have a recap on redox reactions.

Redox reactions are chemical reactions where electrons are transferred from one chemical species to the other. As they do so, their oxidation state changes. A loss of electron by **oxidation reaction** results in the increase of oxidation state of an atom, making it more positively charged. The lost electron is then transferred to the other chemical species by **reduction reaction**, causing a decrease in the oxidation state of an atom, making it less positively charged or negative at times.

In order to balance redox reactions, we should be able to recognize which species undergo reduction or oxidation process. For example, for the reaction

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

The oxidation state of zinc went from (0) to (+2), hence it underwent oxidation reaction. For copper, the oxidation state is reduced to (0) from (+2) by reduction reactions. To balance the reactions, we first split the equation into two half-reactions by combing those with the similar atoms in it. That is

$$Zn \rightarrow Zn^{2+} \qquad \text{(Ox)}$$
$$Cu^{2+} \rightarrow Cu \qquad \text{(Red)}$$

The first step in balancing redox reactions is to balance first the atoms. Since they are already balanced, we then balance them by their charges. Notice that for (Ox), the reactant side do not have any charge at all, while the product side has a net charge of (+2). To balance the charges, we add enough electrons to the side with the highest charge to bring down the charge similar to that of the lowest. For (Ox) two electrons will be added to the product side, and two electrons for the reactant side for (Red). That is,

$$Zn \rightarrow Zn^{2+} + 2\,e^- \qquad \text{(Ox)}$$
$$2\,e^- + Cu^{2+} \rightarrow Cu \qquad \text{(Red)}$$

Finally, we combine the two equations, cancelling out similar terms

$$2\,e^- + Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu + 2\,e^-$$

$$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$$

The next reaction requires more steps, as other atoms such as oxygen and hydronium ions are needed to balance them. Consider the reaction

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

We will notice that the oxidation number of iron increases from (2+) to (3+), thus iron underwent an oxidation process. Consequently, this means that chromate ion underwent reduction process to chromium (III) ion. We can write these two half-reactions as

$$Fe^{2+} \rightarrow Fe^{3+} \qquad \text{(Ox)}$$
$$Cr_2O_7^{2-} \rightarrow Cr^{3+} \qquad \text{(Red)}$$

Then, balance each half-reaction for the number and type of atoms and charges. Add H_2O to balance O atoms first, then add H^+ to balance H atoms.

$$Fe^{2+} \rightarrow Fe^{3+} \qquad \text{(Ox)}$$
$$14\,H^+ + Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O \qquad \text{(Red)}$$

To balance charges, add electrons. The resulting balanced half-reactions are shown as below. Please note that the coefficient should be multiplied to the charge to get the total charge for a chemical species. For (Ox), the reactant side only has a (+2) charge and (+3) charge for the product side. Addition of one electron in the product side will be sufficient to balance the charges. For (Red), to obtain the charge for the reactant side, we multiply the coefficient by the charge, that is $14(+1) + 1(-2) = +12$ charge for the reactant side. For the product side, that is $2(+3) + 7(0) = +6$ charge. Addition of six electrons in the reactant side will make the equations balanced in terms of charges

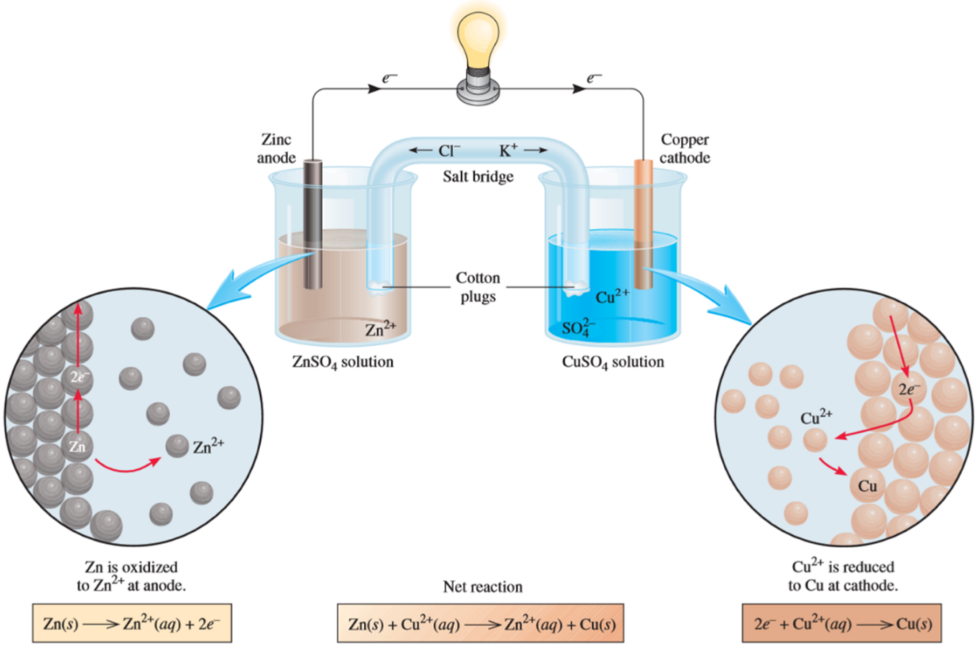
$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \text{(Ox)}$$
$$6\,e^- + 14\,H^+ + Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O \qquad \text{(Red)}$$

Finally, add the two half-reactions together. The electrons must cancel out in the final equation, so you may multiply a factor to any of the two equations. In this case, we multiply (Ox) by six, so the electrons will cancel out eventually. The balanced equation is

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

This reaction is in acidic medium since there are H^+ ions present. To make the reaction in basic medium, just add same amount of OH^- to that of H^+,which will eventually form H_2O molecules. The reaction will then look like

$$6\,Fe^{2+} + 7\,H_2O + Cr_2O_7^{2-} \rightarrow 6\,Fe^{3+} + 2\,Cr^{3+} + 14\,OH^-$$



MNEMONIC GUIDE

OIL RIG	**o**xidation **i**s **l**osing e^-, **r**eduction **i**s **g**aining e^-
LEORA GEROA	**l**osing e^-, **o**xidation, **r**educing **a**gent **g**aining e^-, **r**eduction, **o**xidizing **a**gent

Do not confuse with the oxidized species being called the reducing agent and the reduced species being called the oxidizing agent

Electrochemical Cells

An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

A voltaic, or galvanic, cell is an electrochemical cell in which a spontaneous reaction generates an electric current. An electrolytic cell is an electrochemical cell in which an electric current drives an otherwise nonspontaneous reaction.

A voltaic cell consists of two half-cells that are electrically connected. Each half-cell is the portion of an electrochemical cell in which a half-reaction takes place.

The electrode at which oxidation occurs is called the *anode*. The other electrode at which the reduction occurs is called the *cathode*. The two half-cells are connected by a salt bridge. A salt bridge is a tube on an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants.

Note that by convention, anode is on the left side of the diagram and cathode is on the right side.

MNEMONIC GUIDE	
OXAN REDCAT	**ox**idation at **an**ode, **red**uction at **cat**hode
ABC	cell notation format is **A**node | **B**ridge | **C**athode
A to C	electrons flow from **A**node to **C**athode

Notation for Voltaic Cells

There is a shorthand way of designating particular voltaic cells. For the reaction

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

The cell notation is written in the format

$$\text{Anode Metal} \mid \text{Anode Species} \parallel \text{Cathode Species} \mid \text{Cathode Metal}$$

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

Anode Reaction $Zn \rightarrow Zn^{2+}$

Cathode Reaction $Cu^{2+} \rightarrow Cu$

In this notation, the anode is always written on the left; the cathode is written on the right. The two electrodes are electrically connected by a salt bridge, denoted by two vertical bars ||. The single vertical bar, however, says that there is a phase boundary between the solid terminal and the electrolyte solution. A comma can be used to separate ions present in the same solution. Coefficients, however, are not to be written in the cell notation. When the half-reaction involves a gas, an inert material such as platinum serves as a terminal and as an electrode surface on which the half-reaction occurs. For example, the cathode half-reaction

$$2H^{+} + 2\,e^{-} \rightleftharpoons H_2$$

The notation for the hydrogen electrode as cathode is

$$H^{+}(aq) \mid H_2(g) \mid Pt$$

To write this as an anode, simply reverse the notation

$$Pt \mid H_2(g) \mid H^{+}\,(aq)$$

To fully specify a voltaic cell, it is necessary to give the concentrations of solution or ions and the pressure of gases. In the cell notation, these are written within parenthesis for each species. For example,

$$Zn(s)|\ Zn^{2+}(1.0M)||\ H^{+}(1.0M)|H_2(1.0\ atm)\ |\ Pt$$

Activities and Assessments:

1. Balance the following reactions in both acidic and basic media, identify the oxidation and reduction reactions, and identify the oxidizing and reducing agents.
    a. The oxidation of iodide ion I^- by permanganate ion MnO_4^- in basic solution to yield molecular iodine I_2 and manganese (IV) oxide MnO_2.
    b. $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$
    c. $Sn + NO_3^- \rightarrow SnO_2 + NO_2$
    d. $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$
    e. $Pt\left|Cl^-_{(aq)}\right|Cl_{2(g)}\ \left|\left|NO^-_{3(aq)}\right|NO_{(g)}\right|\ Pt$
    f. $Sn_{(s)}\left|Sn^{2+}_{(aq)}\right|\left|Pb^{2+}_{(aq)}\right|Pb_{(s)}$
    g. $Cd_{(s)}\left|Cd^{2+}_{(aq)}\right|\left|Sb^{3+}_{(aq)}\right|Sb_{(s)}$
    h. $Pt\left|Cu^{+}_{(aq)}, Cu^{2+}_{(aq)}\right|\left|Mg^{2+}_{(aq)}\right|Mg_{(s)}$
    i. $Pt\left|Cr^{3+}_{(aq)}, Cr_2O^{2-}_{7(aq)}\right|\left|ClO^-_{3(aq)}, Cl^-_{(aq)}\right|Pt$
    j. $Mn_{(s)}\left|Mn^{2+}_{(aq)}\right|\left|H^+_{(aq)}\right|H_{2(g)}\ |Pt$

2. Sketch the cell, labeling the anode and cathode and indicating the corresponding electrode reactions. Show the direction of electron flow in the external circuit and the direction of cation movement in the half-cells.
    a. A voltaic cell consists of a silver–silver ion half-cell and a nickel–nickel (II) ion half-cell. Silver ion is reduced during operation of the cell.
    b. A voltaic cell is constructed from a half-cell in which a cadmium rod dips into a solution of cadmium nitrate, $Cd(NO_3)_2$, and another half-cell in which a silver rod dips into a solution of silver nitrate, $AgNO_3$. The two half-cells are connected by a salt bridge. Silver ion is reduced during operation of the voltaic cell.

3. Write the cell reaction for the following:
    a. $Tl\ (s)\ |\ Tl^{+}(aq)\ ||\ Sn^{2+}(aq)\ |\ Sn(s)$
    b. $Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Fe^{3+}(aq),\ Fe^{2+}(aq)\ |\ Pt$
    c. $Cd(s)|\ Cd^{2+}(aq)||\ H^{+}(aq)|H_2(g)\ |\ Pt$

LESSON 8: ELECTROCHEMISTRY
UNIT 2: Standard Cell Potential

Introduction:

Electricity is produced when electrons travel through a circuit. The electrons in the redox electron may do so provided that these are in galvanic cell setup. This chapter focuses on the determination of cell potential under standard conditions and to develop an understanding on the interpretation of the standard reduction potential table.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Determine the cell potential of redox reactions
2. Apply the concept of diagonal rule in determining the spontaneity of redox reacting species.

Course Materials:

A cell potential is a measure of the driving force of the cell reaction. This reaction occurs in the cell as separate half-reactions: and oxidation half-reaction and a reduction half-reaction. The cell potential is the sum of the contributions of oxidation potential and reduction potential, that is

$$E^{\circ}_{cell} = \text{oxidation potential} + \text{reduction potential}$$

A reduction potential is a measure of the tendency for an oxidized species to gain electrons in the reduction half-reaction. The oxidation potential is the negative of the reduction potential on the other hand.

By convention, the standard electromotive force (emf) of the cell (E°_{cell}) is given by

$$E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{an}$$

where both E°_{cat} and E°_{an} are the standard reduction potentials (SRP) of the electrodes in the cathode and the anode whose values can be found in the SRP table. Note that the naught (°) symbol indicates standard states, meaning the concentration of the chemical species are 1.0 M, the pressure is at 1 bar or approximately 1 atmosphere, and the temperature is 25°C. Also, the previously given equation does not mind whether the reaction is reversed or not. Just identify the reactions in the cathode and anode and copy their corresponding E° values. For example, consider the zinc-copper cell

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$$

The half-reactions are

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^{-} \qquad \text{(An)}$$

$$Cu^{2+}(aq) + 2\,e^{-} \rightarrow Cu(s) \qquad \text{(Cat)}$$

The emf of the cell is

$$
\begin{aligned}
E^{\circ}_{cell} &= E^{\circ}_{cat} - E^{\circ}_{an} \\
E^{\circ}_{cell} &= E^{\circ}_{SRP\ Cu^{2+}} - E^{\circ}_{SRP\ Zn^{2+}} \\
E^{\circ}_{cell} &= \ 0.34\,V \ - \ (-0.76V) \\
E^{\circ}_{cell} &= \ 1.10\,V
\end{aligned}
$$

A positive E°_{cell} indicates a voltaic cell system where electron flows spontaneously.

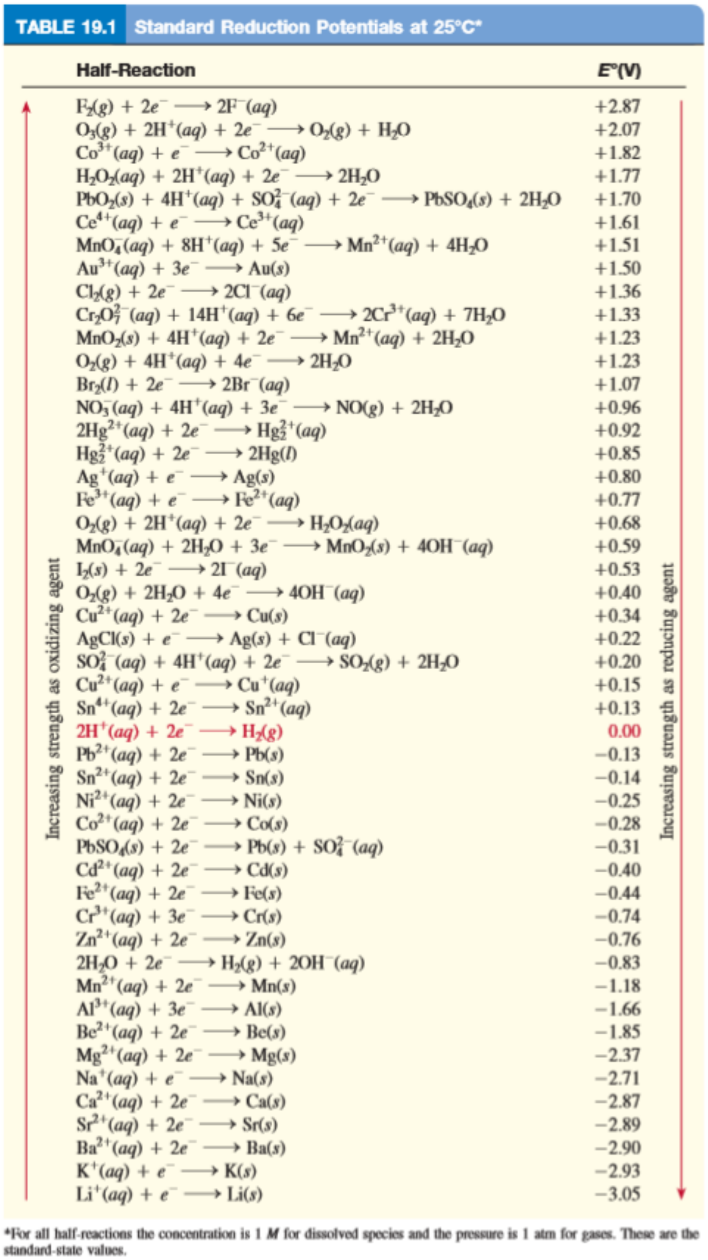


TABLE 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	E°(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

*For all half-reactions the concentration is 1 *M* for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

The table lists standard reduction potentials for several half-cell reactions. The standard hydrogen electrode has an E° value of 0.00 V. Below the SHE the negative standard reduction potentials increase, and above it the positive standard reduction potentials increase. It is important to know the following points about the table in calculations:

1. The more positive E° is, the greater the tendency for the substance to be reduced, and the strength of the substance as an oxidizing agent increases.

   That means if you have a solution with Cu^{2+}/Cu and Sn^{2+}/Sn, copper is most likely to be the cathode for the reaction as it has higher E° than tin, which becomes the anode counterpart.

2. Under standard-state conditions, any species on the left of a given half-cell reaction will react spontaneously with a species that appears on the right of any half-cell reaction located below it in SRP Table. This principle is sometimes called the diagonal rule.

   The diagonal rule can be used to determine which chemical species will react assuming that it undergoes spontaneous reactions, where E°_{cell} is positive in value.

   Consider the SRP table whose species are arranged from highest E° value to the lowest.

$$\begin{aligned}
\mathrm{Ce^{4+}}(aq) + e^- &\longrightarrow \mathrm{Ce^{3+}}(aq) & E^\circ &= +1.61\ \mathrm{V}\\
\mathrm{Ag^{+}}(aq) + e^- &\longrightarrow \mathrm{Ag}(s) & E^\circ &= +0.80\ \mathrm{V}\\
\mathrm{Hg_2{}^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{2Hg}(l) & E^\circ &= +0.80\ \mathrm{V}\\
\mathrm{Sn^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{Sn}(s) & E^\circ &= -0.14\ \mathrm{V}\\
\mathrm{Ni^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{Ni}(s) & E^\circ &= -0.24\ \mathrm{V}\\
\mathrm{Al^{3+}}(aq) + 3e^- &\longrightarrow \mathrm{Al}(s) & E^\circ &= -1.68\ \mathrm{V}
\end{aligned}$$

   Species on the left side will react spontaneously to that on the right side below it. That means, Ce^{4+} will serve as the cathode that will react spontaneously with anodes containing $Ag(s), Hg(l), Sn(s), Ni(s)$, and $Al(s)$ and their corresponding ions. The same is true for others provided that diagonal rule is observed.

   Question 1: Will Sn reduce Ag^{+} to Ag?

$$\begin{aligned}
\mathrm{Ce^{4+}}(aq) + e^- &\longrightarrow \mathrm{Ce^{3+}}(aq) & E^\circ &= +1.61\ \mathrm{V}\\
\mathrm{Ag^{+}}(aq) + e^- &\longrightarrow \mathrm{Ag}(s) & E^\circ &= +0.80\ \mathrm{V}\\
\mathrm{Hg_2{}^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{2Hg}(l) & E^\circ &= +0.80\ \mathrm{V}\\
\mathrm{Sn^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{Sn}(s) & E^\circ &= -0.14\ \mathrm{V}\\
\mathrm{Ni^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{Ni}(s) & E^\circ &= -0.24\ \mathrm{V}\\
\mathrm{Al^{3+}}(aq) + 3e^- &\longrightarrow \mathrm{Al}(s) & E^\circ &= -1.68\ \mathrm{V}
\end{aligned}$$

By diagonal rule, the reaction is possible. Also, if Ag^+ will serve as the cathode for the anode containing Sn^{2+}/Sn, the E°_{cell} can be computed as

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cat} - E^\circ_{an} \\ E^\circ_{cell} &= E^\circ_{SRP\ Ag^+} - E^\circ_{SRP\ Sn^{2+}} \\ E^\circ_{cell} &= 0.80\ V - (-0.14\ V) \\ E^\circ_{cell} &= 0.94\ V \end{aligned}$$

A positive E°_{cell} value indicates a spontaneous reaction.

3. Changing the stoichiometric coefficients of a half-cell reaction does not affect the value of E° because electrode potentials are intensive properties.

   A reduction potential

   $$Li^+(aq) + e^- \rightarrow Li(s) \qquad (-3.05\ V)$$

   would have the same E° value as

   $$3\ Li^+(aq) + 3\ e^- \rightarrow 3\ Li(s) \qquad (-3.05\ V)$$

4. The sign of E° changes but its magnitude remains the same when we reverse a reaction.

   All reactions on the SRP table are the reduction potentials. If you want to determine the oxidation potential, you just have to reverse the equation and reverse the sign of the E°. For the reduction potential

   $$Li^+(aq) + e^- \rightarrow Li(s) \qquad (-3.05\ V)$$

   The oxidation potential is written as

   $$Li(s) \rightarrow Li^+(aq) + e^- \qquad (+3.05\ V)$$

5. The positive E°_{cell} means that the reaction is galvanic cell / the reaction is spontaneous. A negative value denotes that the reaction is electrolytic.

Activities and Assessments:

1. Determine the E°_{cell} values for the following:
   a. $Tl\ (s)\ |\ Tl^+(aq)\ ||\ Sn^{2+}(aq)\ |\ Sn(s)$
   b. $Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Fe^{3+}(aq),\ Fe^{2+}(aq)\ |\ Pt$
   c. $Cd(s)|\ Cd^{2+}(aq)||\ H^+(aq)|H_2(g)\ |\ Pt$
   d. $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$
   e. $Sn + NO_3^- \rightarrow SnO_2 + NO_2$
   f. $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$
   g. The oxidation of iodide ion I^- by permanganate ion MnO_4^- in basic solution to yield molecular iodine I_2 and manganese (IV) oxide MnO_2.

2. For the following half-reactions, answer the following questions below

$$\begin{aligned}
\mathrm{Co^{3+}}(aq) + e^- &\longrightarrow \mathrm{Co^{2+}}(aq) & E^\circ &= +1.953\ \mathrm{V}\\
\mathrm{Fe^{3+}}(aq) + e^- &\longrightarrow \mathrm{Fe^{2+}}(aq) & E^\circ &= +0.769\ \mathrm{V}\\
\mathrm{I_2}(aq) + 2e^- &\longrightarrow 2\mathrm{I^-}(aq) & E^\circ &= +0.534\ \mathrm{V}\\
\mathrm{Pb^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{Pb}(s) & E^\circ &= -0.127\ \mathrm{V}\\
\mathrm{Cd^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{Cd}(s) & E^\circ &= -0.402\ \mathrm{V}\\
\mathrm{Mn^{2+}}(aq) + 2e^- &\longrightarrow \mathrm{Mn}(s) & E^\circ &= -1.182\ \mathrm{V}
\end{aligned}$$

a. Which is the weakest reducing agent?
b. Which is the strongest reducing agent?
c. Which is the strongest oxidizing agent?
d. Which is the weakest oxidizing agent?
e. Will Pb reduce Fe^{3+} to Fe^{2+}?
f. Will I^- reduce Pb^{2+} to Pb?
g. Which ion/s can be reduced by Pb?
h. Which metal/s can be oxidized by Fe^{3+}?

LESSON 8: ELECTROCHEMISTRY

UNIT 3: Thermodynamics in Electrochemistry, Concentration Effects on E°_{cell}

Introduction:

Electrochemical reactions with positive cell potential value occurs spontaneously, while those with negative values do otherwise. In this chapter, we will correlate the ideas of cell potentials and the spontaneity (by Gibbs Free Energy) and the use of chemical equilibrium concept to derive equations for nonstandard conditions.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Determine the correlation of Gibbs Free Energy and the equilibrium constant on the spontaneity of redox reactions.
2. Derive and apply the equations for non-standard state: the Nernst equation.

Course Materials:

Work is needed to move electrons in a wire. An electric charge moves from a point at high electrical potential (high electrical pressure) to a point at low electric potential (low electrical pressure). The work needed to move an electric charge through a conductor depends on the total charge moved and the potential difference. Potential difference is the difference in electric potential (electrical pressure) between two points. This is measured in volts. The electrical work expended in moving a charge through a conductor is

$$\text{electrical work} = \text{charge} \times \text{potential difference}$$

Corresponding SI units for the terms in this equation is $\text{Joules} = \text{coulombs (C)} \times \text{volts (V)}$

The total charge is determined by the number of electrons that pass through the cell, so we have

$$\text{total charge } (Q) = (\#\text{ of } e^-) \times (\text{charge of one e}^-)$$

In general, it is more convenient to express the total charge in molar quantities. The Faraday constant (F) is the magnitude of charge per mole of electrons and is equal to 96485 C/mol e^-, sometimes approximated as 96500 C/mol e^- as the deviation is negligible anyway.

Therefore, the total charge (Q) can now be expressed as nF, where n is the number of moles of electrons exchanged between the reducing agent and the oxidizing agent in the overall redox equation.

The measured emf (E°_{cell}) is the maximum voltage the cell can achieve. It is given by the electrical work done (w_{ele}) divided by the total charge; that is,

$$E^{\circ}_{cell} = -\frac{w_{ele}}{Q}$$

$$E^{\circ}_{cell} = -\frac{w_{ele}}{nF}$$

$$w_{ele} = -nFE^{\circ}_{cell}$$

Note that the negative sign indicates that the electrical work is done by the system (galvanic cell) on the surroundings.

In previous chapters, free energy is defined as the energy available to do work. Specifically, the change in free energy ΔG represents the maximum amount of useful work that can be obtained in a reaction:

$$\Delta G = w_{max} = w_{ele}$$

Therefore,

$$\Delta G = -nFE_{cell}$$

At standard conditions

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

Now, E°_{cell} can be related to the equilibrium constant K of a redox reaction given by the equation

$$\Delta G^{\circ} = -RT\ln K$$

Combining the ΔG° expressions, we obtain

$$-nFE^{\circ}_{cell} = -RT\ln K$$

Solving for E°_{cell}

$$E^{\circ}_{cell} = \frac{RT}{nF}\ln K$$

When $T = 298\ K$, the previous expression can be simplified as

$$E^{\circ}_{cell} = \frac{8.314\frac{J}{mol \cdot K} \times\ 298\ K}{n\left(96500\frac{J}{V \cdot mol}\right)}\ln K$$

$$E^{\circ}_{cell} = \frac{0.0257\ V}{n}\ln K$$

or

$$E^{\circ}_{cell} = \frac{0.0592\ V}{n}\log K$$

The table below is useful when interpreting the spontaneity and the direction of the reactions.

ΔG°	K	E°_{cell}	*Reaction under Standard-State Conditions*
Negative	>1	Positive	Spontaneous; will proceed to products
Zero (0)	=1	Zero (0)	At equilibrium
Positive	<1	Negative	Nonspontaneous; will proceed to reactants

Sample Problems

1. Calculate the standard free-energy change under standard conditions for the reaction $Au(s) + Ca^{2+} \rightarrow Au^{3+} + Ca(s)$

   To solve for ΔG° of the reaction, we solve first for the E°_{cell} of the reaction. Au^{3+}/Au is the anode and Ca^{2+}/Ca is the cathode for this reaction so,

$$E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{an}$$
$$E^{\circ}_{cell} = (-2.87\ V) - (1.50\ V)$$
$$E^{\circ}_{cell} = -4.37\ V$$

   Since the E°_{cell} is negative in value, we expect a positive ΔG° value and a K value less than one (1), approaching zero. Note that six (6) electrons are needed as the final equation before cancelling electrons is written as $6\,e^{-} + 2\,Au(s) + 3\,Ca^{2+} \rightarrow 2\,Au^{3+} + 3\,Ca(s) + 6\,e^{-}$.

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$
$$\Delta G^{\circ} = -(6\ \text{mol}\ e^{-}) \times 96500 \frac{C}{\text{mol}\ e^{-}} \times (-4.37\ V)$$
$$\Delta G^{\circ} = 2.53 \times 10^{6}\ C \cdot V$$
$$\Delta G^{\circ} = 2.53 \times 10^{6}\ J$$

   Now solving for K, we can use the shortcut equation

$$E^{\circ}_{cell} = \frac{0.0257\ V}{n} \ln K$$
$$\ln K = \frac{E^{\circ}_{cell} \cdot n}{0.0257\ V}$$
$$K = e^{\left(\frac{E^{\circ}_{cell} \cdot n}{0.0257\ V}\right)}$$
$$K = e^{\left(\frac{-4.37\ V \cdot 6}{0.0257\ V}\right)}$$
$$K \approx 0$$

2. Determine the E°_{cell} and the equilibrium constant K under standard conditions for the reaction $Sn(s) + Cu^{2+}(aq) \rightleftharpoons Sn^{2+}(aq) + Cu^{+}(aq)$

   Note than Sn^{2+}/Sn is the anode for the reaction and Cu^{2+}/Cu^{+} is the cathode. Solve for E°_{cell}

$$E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{an}$$

$$E^{\circ}_{cell} = (0.15\ V) - (-0.14\ V)$$

$$E^{\circ}_{cell} = 0.29\ V$$

A positive E°_{cell} value indicates a K value greater than one (1).

$$E^{\circ}_{cell} = \frac{0.0257\ V}{n} \ln K$$
$$\ln K = \frac{E^{\circ}_{cell} \cdot n}{0.0257\ V}$$
$$K = e^{\left(\frac{E^{\circ}_{cell} \cdot n}{0.0257\ V}\right)}$$
$$K = e^{\left(\frac{0.29\ V \cdot 2}{0.0257\ V}\right)}$$
$$K = 6.32 \times 10^{9}$$

Concentration Effects on E°_{cell}

Recall that the free-energy change (ΔG) is related to the standard free-energy change (ΔG°) by the following equation

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

Here Q is the thermodynamic reaction quotient. The reaction quotient has the form of the equilibrium constant, except that the concentrations and gas pressures are those that exist in a reaction mixture at a given instant. You can apply this equation to a voltaic cell. In that case, the concentrations and gas pressures are those that exist in the cell at an instant. If you substitute $\Delta G = -nFE_{cell}$ and $\Delta G^{\circ} = -nFE^{\circ}_{cell}$ into this equation, we obtain

$$-nFE_{cell} = -nFE^{\circ}_{cell} + RT \ln Q$$

Rearranging in terms of cell potential, this results to the Nernst Equation, an equation relating the cell potential to its standard cell potential and the reaction quotient.

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln Q$$

or

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303\ RT}{nF} \log Q$$

At $T = 298\ K$,

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0257\ V}{n} \ln Q$$

or

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592\ V}{n} \log Q$$

The Nernst equation enables us to calculate E_{cell} as a function of reactant and product concentrations in a redox reaction. For example, for the reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

The Nernst equation for this cell at 25°C can be written as

$$E_{cell} = 1.10\,V\ - \frac{0.0257\,V}{2} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Sample Problems

1. Predict whether the following reaction would proceed spontaneously at 298 K $Co(s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe(s)$ given that $[Co^{2+}] = 0.25\,M$ and $[Fe^{2+}] = \ 0.94\,M$.

   One way to determine the spontaneity of this reaction is to see if E_{cell} is positive in value or not. Since this is a non-standard condition as the concentrations are not all equal to 1.0 M, we use the Nernst Equation.

   We solve first for E°_{cell}. In this reaction, Co^{2+}/Co serves as the anode and Fe^{2+}/Fe serves as the cathode, thus

   $$\begin{aligned} E^{\circ}_{cell} &= E^{\circ}_{cat} - E^{\circ}_{an} \\ E^{\circ}_{cell} &= (-0.44\,V) - (-0.28\,V) \\ E^{\circ}_{cell} &= -0.16\,V \end{aligned}$$

   We ended up with a negative E°_{cell} value but remember that it is not the final answer as the reaction is taking place in nonstandard conditions. We write the Nernst equation for this reaction as

   $$\begin{aligned} E_{cell} &= E^{\circ}_{cell} - \frac{0.0257\,V}{n} \ln Q \\ E_{cell} &= (-0.16\,V) - \frac{0.0257\,V}{2} \ln \frac{[Co^{2+}]}{[Fe^{2+}]} \end{aligned}$$

   Solving for E_{cell}

   $$\begin{aligned} E_{cell} &= (-0.16\,V) - \frac{0.0257\,V}{2} \ln \frac{(0.25)}{(0.94)} \\ E_{cell} &= -0.14\,V \end{aligned}$$

   Observe that concentrations can affect E_{cell}. Since we arrived with yet still another negative E_{cell} value, the reaction is still nonspontaneous.

2. In a certain experiment, the emf of the cell is found to be 0.54 V at 25°C. Suppose that $[Zn^{2+}] = 2.5\,M$ and $P_{H_2} = 1.0\ \mathrm{atm}$, what is the pH of the solution?

   $$Zn(s) + 2\,H^{+}(?\ M) \rightarrow Zn^{2+}(2.5\,M) + H_2\ (1.0\ atm)$$

We solve first for the E°_{cell} where Zn^{2+}/Zn is our anode and H^+/H_2 is our cathode.

$$E^\circ_{cell} = E^\circ_{cat} - E^\circ_{an}$$
$$E^\circ_{cell} = (0\ V) - (-0.76\ V)$$
$$E^\circ_{cell} = 0.76\ V$$

Next is to write the Nernst Equation for the given reaction.

$$E_{cell} = E^\circ_{cell} - \frac{0.0257\ V}{n} \ln Q$$
$$0.54\ V = (0.76\ V) - \frac{0.0257\ V}{2} \ln \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$$

Rearrange the equation to obtain $[H^+]$ only, then pH

$$0.54\ V = (0.76\ V) - \frac{0.0257\ V}{2} \ln \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$$

$$\frac{-2(0.54\ V - 0.76\ V)}{0.0257\ V} = \ln \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$$

$$\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2} = e^{\frac{-2(0.54\ V - 0.76\ V)}{0.0257\ V}}$$

$$[H^+] = \sqrt{\frac{[Zn^{2+}]P_{H_2}}{e^{\frac{-2(0.54\ V - 0.76\ V)}{0.0257\ V}}}}$$

$$[H^+] = \sqrt{\frac{2.5 \cdot 1}{e^{\frac{-2(0.54\ V - 0.76\ V)}{0.0257\ V}}}}$$

$$[H^+] = 3.03 \times 10^{-4} M$$

$$\text{p}H = -\log[H^+]$$

$$\text{p}H = 3.52$$

Activities and Assessments:

1. What is the emf of a galvanic cell consisting of a Cd^{2+}/Cd half-cell and a $Pt/H^+/H_2$ half-cell if $[Cd^{2+}] = 0.20\ M, [H^+] = 0.16\ M$, and $P_{H_2} = 0.80\ \text{atm}$?

2. Consider the cell diagram $Mg(s)|MgSO_4(0.40\ M)||NiSO_4(0.60\ M)|Ni(s)$. Calculate the cell voltage at 25°C. How does the cell voltage change when:
   a. $[Mg$2+] is decreased by a factor of 4
   b. $[Ni$2+] is decreased by a factor of 3

3. Consider the reaction at 25°C
$$MnO_{2(s)} + 4\ H^+_{(aq)} + 2\ Br^-_{(aq)} \rightarrow Mn^{2+}_{(aq)} + Br_{2(l)} + 2H_2O_{(l)}$$
At what pH is the voltage zero if all other species are at standard conditions?

LESSON 8: ELECTROCHEMISTRY
UNIT 4: Batteries and Corrosion

Introduction:

The world is heavily dependent on batteries, whether be it on your cellphone, laptops, and electric vehicles to name a few. In this chapter we will identify the common types of batteries and the redox reactions happening in it. Also, we will discuss the corrosion phenomena.

Learning Objectives:

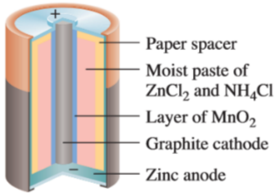
After successful completion of this lesson, the students are expected to:

1. Recognize and understand how batteries work and how their applications.
2. Explain the corrosion process and ways to protect metals from it.

Course Materials:

A battery is a galvanic cell, or a series of combined galvanic cells, that can be used as a source of direct electric current at a constant voltage. Although the operation of a battery is similar in principle to that of the galvanic cells, a battery has the advantage of being completely self-contained and requiring no auxiliary components such as salt bridges.

Dry Cell Battery



The most common dry cell, that is, a cell without a fluid component, is the Leclanché cell used in flashlights and transistor radios. The anode of the cell consists of a zinc can or container that is in contact with manganese dioxide (MnO_2) and an electrolyte. The electrolyte consists of ammonium chloride and zinc chloride in water, to which starch is added to thicken the solution to a pastelike consistency so that it is less likely to leak A carbon rod serves as the cathode, which is immersed in the electrolyte in the center of the cell. The cell reactions are

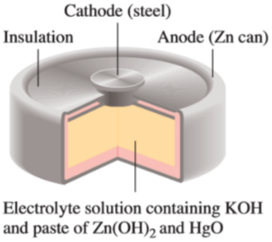
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^- \qquad \text{(An)}$$

$$2\,NH_4^+(aq) + 2\,MnO_2(s) + 2\,e^- \rightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l) \qquad \text{(Cat)}$$

$$Zn(s) + 2\,NH_4^+(aq) + 2\,MnO_2(s) \rightarrow Zn^{2+}(aq) + 2\,NH_3(aq) + H_2O(l\,) + \ Mn_2O_3(s)$$

This equation is an oversimplification of a complex process. The voltage produced by a dry cell is about 1.5 V.

Mercury Battery



The mercury battery is used extensively in medicine and electronic industries and is more expensive than the common dry cell. Contained in a stainless steel cylinder, the mercury battery consists of a zinc anode (amalgamated with mercury) in contact with a strongly alkaline electrolyte containing zinc oxide and mercury(II) oxide. The cell reactions are

$$\begin{array}{rr} Zn(Hg) + 2\,OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2\,e^- & \text{(An)} \\ HgO(s) + H_2O(l) + 2\,e^- \rightarrow Hg(l) + 2\,OH^-(aq) & \text{(Cat)} \\ \hline Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l) & \end{array}$$

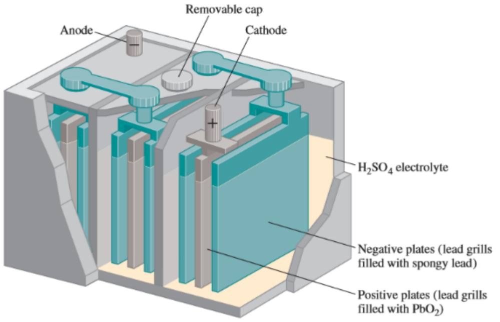
Because there is no change in electrolyte composition during operation—the overall cell reaction involves only solid substances—the mercury battery provides a more constant voltage (1.35 V) than the Leclanché cell. It also has a considerably higher capacity and longer life. These qualities make the mercury battery ideal for use in pacemakers, hearing aids, electric watches, and light meters.

Lead Storage Battery

The lead storage battery commonly used in automobiles consists of six identical cells joined together in series. Each cell has a lead anode and a cathode made of lead dioxide (PbO_2) packed on a metal plate Both the cathode and the anode are immersed in an aqueous solution of sulfuric acid, which acts as the electrolyte. The cell reactions are

$$\begin{array}{rr} Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\,e^- & \text{(An)} \\ PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2\,e^- \rightarrow PbSO_4(s) + 2\,H_2O(l) & \text{(Cat)} \\ \hline Pb(s) + PbO_2(s) + 4\,H^+(aq) + 2\,SO_4^{2-}(aq) \rightarrow 2\,PbSO_4(s) + 2\,H_2O(l) & \end{array}$$

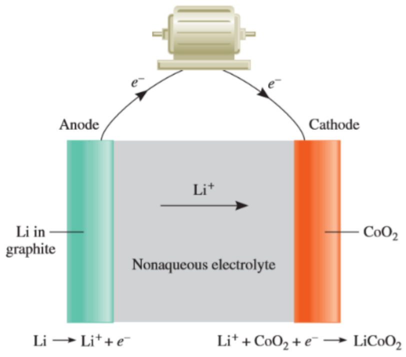
Under normal operating conditions, each cell produces 2 V; a total of 12 V from the six cells is used to power the ignition circuit of the automobile and its other electrical systems. The lead storage battery can deliver large amounts of current for a short time, such as the time it takes to start up the engine.



Unlike the Leclanché cell and the mercury battery, the lead storage battery is rechargeable. Recharging the battery means reversing the normal electrochemical reaction by applying an external voltage at the cathode and the anode. (This kind of process is called electrolysis). The reactions that replenish the original materials are

$$\begin{array}{rr} PbSO_4(s) + 2\,e^- \rightarrow Pb(s) + SO_4^{2-}(aq) & \text{(An)} \\ PbSO_4(s) + 2\,H_2O(l) \rightarrow PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2\,e^- & \text{(Cat)} \\ \hline 2\,PbSO_4(s) + 2\,H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4\,H^+(aq) + 2\,SO_4^{2-}(aq) & \end{array}$$

Lithium-Ion Battery



The anode is made of a conducting carbonaceous material, usually graphite, which has tiny spaces in its structure that can hold both Li atoms and Li^+ ions. The cathode is made of a transition metal oxide such as CoO_2, which can also hold Li^+ ions.

Because of the high reactivity of the metal, nonaqueous electrolyte (organic solvent plus dissolved salt) must be used. During the discharge of the battery, the half-cell reactions are

$$\begin{array}{cr} Li(s) \rightarrow Li^+ + e^- & \text{(An)} \\ Li^+ + CoO_2 + e^- \rightarrow LiCoO_2(s) & \text{(Cat)} \\ \hline Li(s) + CoO_2 \rightarrow LiCoO_2(s) & E_{cell} = 3.4\,V \end{array}$$

The advantage of the battery is that lithium has the most negative standard reduction potential and hence the greatest reducing strength. Furthermore, lithium is the lightest metal so that only 6.941 g of Li (its molar mass) are needed to produce 1 mole of electrons. A lithium-ion battery can be recharged literally hundreds of times without deterioration. These desirable characteristics make it suitable for use in cellular telephones, digital cameras, and laptop computers.

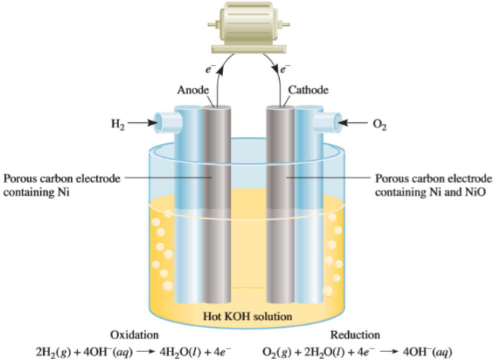
Fuel Cells

In its simplest form, a hydrogen-oxygen fuel cell consists of an electrolyte solution, such as potassium hydroxide solution, and two inert electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartments where the following reactions take place:

$$\begin{array}{cr} 2\,H_2(g) + 4\,OH^-(aq) \rightarrow 4\,H_2O(l) + 4\,e^- & \text{(An)} \\ O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq) & \text{(Cat)} \\ \hline 2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l) & \end{array}$$

The standard emf can be computed as follows

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cat} - E^\circ_{an} \\ &= 0.40\,V - (-0.83\,V) \\ &= 1.23\,V \end{aligned}$$



Thus, the cell reaction is spontaneous under standard-state conditions. Note that the reaction is the same as the hydrogen combustion reaction, but the oxidation and reduction are carried out separately at the anode and the cathode. Like platinum in the standard hydrogen electrode, the electrodes have a twofold function. They serve as electrical conductors, and they provide the necessary surfaces for the initial decomposition of the molecules into atomic species, prior to electron transfer. They are electrocatalysts. Metals such as platinum, nickel, and rhodium are good electrocatalysts.

In addition to the H_2-O_2 system, a few other fuel cells have been developed. Among these is the propane-oxygen fuel cell. The half-cell reactions are

$$\begin{array}{cr} C_3H_8(g) + 6\,H_2O(l) \rightarrow 3\,CO_2\,(g) + 20\,H^+(aq) + 20\,e^- & \text{(An)} \\ 5\,O_2(g) + 20\,H^+(aq) + 20\,e^- \rightarrow 10\,H_2O(l) & \text{(Cat)} \\ \hline C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l) & \end{array}$$

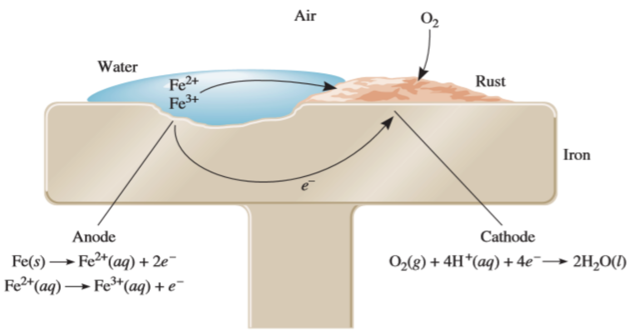
Unlike batteries, fuel cells do not store chemical energy. Reactants must be constantly resupplied, and products must be constantly removed from a fuel cell. In this respect, a fuel cell resembles an engine more than it does a battery.

Properly designed fuel cells may be as much as 70 percent efficient, about twice as efficient as an internal combustion engine. In addition, fuel-cell generators are free of the noise, vibration, heat transfer, thermal pollution, and other problems normally associated with conventional power plants. Nevertheless, fuel cells are not yet in widespread use. A major problem lies in the lack of cheap electrocatalysts able to function efficiently for long periods of time without contamination. The most successful application of fuel cells to date has been in space vehicles.

Corrosion

Corrosion is the term usually applied to the deterioration of metals by an electrochemical process.

By far the most familiar example of corrosion is the formation of rust on iron. Oxygen gas and water must be present for iron to rust. Although the reactions involved are quite complex and not completely understood, the main steps are believed to be as follows. A region of the metal's surface serves as the anode, where oxidation occurs:



$$Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-$$

The electrons given up by iron reduce atmospheric oxygen to water at the cathode, which is another region of the same metal's surface:

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$$

The overall redox reaction is

$$2\,Fe(s) + O_2(g) + 4\,H^+(aq) \rightarrow 2\,Fe^{2+}(aq) + 2\,H_2O(l)$$

The standard emf for this process is

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cat} - E^\circ_{an} \\ &= 1.23\,V - (-0.44\,V) \\ &= 1.67\,V \end{aligned}$$

The Fe^{2+} formed at the anode are further oxidized by oxygen:

$$4\,Fe^{2+}(aq) + O_2(g) + (4+2x)H_2O(l) \rightarrow 2\,Fe_2O_3 \cdot x\,H_2O(s) + 8\,H^+(aq)$$

The hydrated form of iron (III) oxide is known as rust.

Metallic corrosion is not limited to iron. Consider aluminum, a metal used to make many useful things, including airplanes and beverage cans. Aluminum has a much greater tendency to oxidize than iron does as Al has a more negative standard reduction potential than Fe. Based on this fact alone, we might expect to see airplanes slowly corrode away in rainstorms, and soda cans transformed into piles of corroded aluminum. These processes do not occur because the layer of insoluble aluminum oxide (Al_2O_3) that forms on its surface when the metal is exposed to air serves to protect the aluminum underneath from further corrosion. The rust that forms on the surface of iron, however, is too porous to protect the underlying metal.

Coinage metals such as copper and silver also corrode, but much more slowly. In normal atmospheric exposure, copper forms a layer of copper carbonate ($CuCO_3$), a green substance also called patina, that protects the metal underneath from further corrosion. Likewise, silverware that comes into contact with foodstuffs develops a layer of silver sulfide (Ag_2S).

Several methods have been devised to protect metals from corrosion. Most of these methods are aimed at preventing rust formation. The most obvious approach is to coat the metal surface with paint. However, if the paint is scratched, pitted, or dented to expose even the smallest area of bare metal, rust will form under the paint layer. The surface of iron metal can be made inactive by a process called passivation. A thin oxide layer is formed when the metal is treated with a strong oxidizing agent such as concentrated nitric acid. A solution of sodium chromate is often added to cooling systems and radiators to prevent rust formation.

The tendency for iron to oxidize is greatly reduced when it is alloyed with certain other metals. For example, in stainless steel, an alloy of iron and chromium, a layer of chromium oxide forms that protects the iron from corrosion.

An iron container can be covered with a layer of another metal such as tin or zinc. A “tin” can is made by applying a thin layer of tin over iron. Rust formation is prevented if the tin layer remains intact. However, once the surface has been scratched, rusting occurs rapidly. If we look up the standard reduction potentials, according to the diagonal rule, we find that iron acts as the anode and tin as the cathode in the corrosion process:

$$Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s) \qquad E^\circ = -0.14\,V$$
$$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s) \qquad E^\circ = -0.44\,V$$

The protective process is different for zinc-plated, or galvanized, iron. Zinc is more easily oxidized than iron

$$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s) \qquad E^\circ = -0.76\,V$$

So even if a scratch exposes the iron, the zinc is still attacked. In this case, the zinc metal serves as the anode and the iron is the cathode.

Cathodic protection is a process in which the metal that is to be protected from corrosion is made the cathode in what amounts to a galvanic cell

Activities and Assessments:

1. Investigate on the use of organic polymer materials in making batteries. You may use journal articles and news features. Describe the concept of redox systems in such type of batteries.

2. Assess the risks of corrosion and how are these mitigated in the industry.

LESSON 8: ELECTROCHEMISTRY
UNIT 5: Electrolysis

Introduction:

Nonspontaneous redox reactions can occur provided that electricity is passed through it. This concept is used primarily in electroplating metals. An in depth understanding of it will be discussed in this chapter.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Demonstrate how to make nonspontaneous redox reactions possible through electrolysis.
2. Demonstrate the quantitative aspects of electrolysis and its application in electroplating.

Course Materials:

In contrast to spontaneous redox reactions, which result in the conversion of chemical energy into electrical energy, electrolysis is the process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur. An electrolytic cell is an apparatus for carrying out electrolysis.

Electrolysis of Molten Sodium Chloride

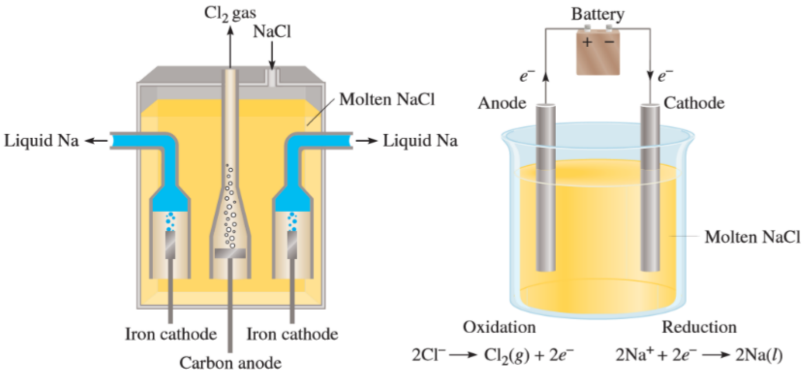
In its molten state, sodium chloride, an ionic compound, can be electrolyzed to form sodium metal and chlorine. The figure below is the Downs cell which is used for large-scale electrolysis of NaCl. The electrolytic cell contains a pair of electrodes connected to the battery. The battery serves as an "electron pump," driving electrons to the cathode, where reduction occurs, and withdrawing electrons from the anode, where oxidation occurs. The reactions at the electrodes are

$$2\,Cl^-(l) \rightarrow Cl_2(g) + 2\,e^- \qquad \text{(An)}$$

$$2\,Na^+(l) + 2\,e^- \rightarrow 2\,Na(l) \qquad \text{(Cat)}$$

$$2\,Na^+(l) + 2\,Cl^-(l) \rightarrow 2\,Na(l) + Cl_2(g)$$

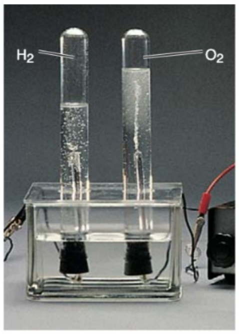
This process is a major source of pure sodium metal and chlorine gas. Theoretical estimates show that the $E°$ value for the overall process is about - 4 V, which means that this is a nonspontaneous process.



Electrolysis of Water

Water in a beaker under atmospheric conditions (1 atm and 25°C) will not spontaneously decompose to form hydrogen and oxygen gas because the standard free-energy change for the reaction is a large positive quantity

$$2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) \qquad \Delta G^{\circ} = 474.4\ kJ \cdot mol^{-1}$$



However, this reaction can be induced. This electrolytic cell consists of a pair of electrodes made of a nonreactive metal, such as platinum, immersed in water. When the electrodes are connected to the battery, nothing happens because there are not enough ions in pure water to carry much of an electric current. On the other hand, the reaction occurs readily in a 0.1 M H_2SO_4 solution because there are enough ions to conduct electricity. Immediately, gas bubbles begin to appear at both electrodes.

The overall reaction is given as

$$\begin{array}{rr} 2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- & \text{(An)} \\ H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g) & \text{(Cat)} \\ \hline 2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) & \end{array}$$

Quantitative Aspect of Electrolysis

The quantitative treatment of electrolysis was developed primarily by Faraday. He observed that the mass of product formed (or reactant consumed) at an electrode is proportional to both the amount of electricity transferred at the electrode and the molar mass of the substance in question.

In an electrolysis experiment, we generally measure the current (in amperes, A) that passes through an electrolytic cell in a given period of time. The relationship between charge (in coulombs, C) and current is

$$\text{Charge (C)} = \text{Electrical current (A)} \times \text{time (s)}$$
$$Q = It$$

that is, a coulomb is the quantity of electrical charge passing any point in the circuit in one (1) second when the current is 1 ampere.

Recall also that the charge is the product of Faraday's constant and the moles of electrons

$$Q = n_eF$$

Thus

$$It = n_eF$$

Sample Problems

1. Consider the electrolysis of $CaCl_2$ forming $Ca\ (s)$ and Cl_2 gas. Suppose a current of 0.452 A is passed through the cell for 1.50 h. How much product will be formed at the anode and at the cathode?

First, we write down the half-reactions and the overall reaction for the electrolysis process. The reaction with the most positive E° value will be our anode reaction this time, this is in contrast to that of the galvanic cell where the most positive E°reaction corresponds to the cathode reaction. Do not cancel out electrons.

$$2\,Cl^{-}(aq) \rightarrow Cl_2(g) + 2\,e^{-} \qquad \text{(An)}$$
$$Ca^{2+}(aq) + 2\,e^{-} \rightarrow Ca(l) \qquad \text{(Cat)}$$

$$2\,e^{-} + Ca^{2+}(aq) + 2\,Cl^{-} \rightarrow Ca(l) + Cl_2(g) + 2\,e^{-}$$

Using the information given earlier, we solve for the n_e using the formula $It = n_eF$

$$n_e = \frac{It}{F}$$
$$n_e = \frac{0.452\,A \times \left(1.5\text{ h} \times \frac{3600\text{ s}}{1\text{ hr}}\right)}{96500\,C}$$
$$n_e = 0.0253\text{ mol}$$

The masses of Cl_2 and Ca produced can now be solved using stoichiometry, as given in the overall equation. We solve first for the equivalent moles for each substance using n_e and use their corresponding molar masses to arrive with the answer.

$$n_{Ca} = n_e \times \frac{1\text{ mol }Ca}{2\text{ mol }e^{-}} = 0.0253\text{ mol} \times \frac{1}{2} = 0.0126\text{ mol}$$

$$m_{Ca} = n_{Ca} \times MM_{Ca} = 0.126\text{ mol} \times 40.08\text{ g}\cdot\text{mol}^{-} = \mathbf{0.507\ g\ Cl_2}$$

$$n_{Cl_2} = n_e \times \frac{1\text{ mol }Cl_2}{2\text{ mol }e^{-}} = 0.0253\text{ mol} \times \frac{1}{2} = 0.0126\text{ mol}$$

$$m_{Cl_2} = n_{Cl_2} \times MM_{Cl_2} = 0.126\text{ mol} \times 70.90\text{ g}\cdot\text{mol}^{-} = \mathbf{0.897\ g\ Cl_2}$$

2. A constant electric current deposits 365 mg of silver in 216 min from an aqueous silver nitrate solution. What is the current?

   This is an example of electroplating process. An electric current is applied to the metal ion solution in order to reduce the metal to its metallic form. For this problem, the present metal ion is Ag^{+} from $Ag(NO_3)$, hence the reaction is

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$

   We use the formula $It = n_eF$ to solve for the current. However, the equation requires the moles of electrons. To solve for the moles of electrons, we convert the mass of $Ag(s)$ to moles of electrons using the stoichiometry in the previous equation as follows

$$n_e = n_{Ag} \times \frac{1\text{ mol }e^{-}}{1\text{ mol }Ag} = \frac{m_{Ag}}{MM_{Ag}} \times \frac{1\text{ mol }e^{-}}{1\text{ mol }Ag}$$
$$n_e = \frac{0.365\,g}{107.868\,g\text{ mol}^{-}} \times \frac{1\text{ mol }e^{-}}{1\text{ mol }Ag} = 3.38 \times 10^{-3}\text{ mol}$$

To solve for the current,

$$I = \frac{n_e F}{t} = \frac{(3.38 \times 10^{-3}\text{mol}) \times 96500\ C \cdot \text{mol}^{-}}{216\ \text{min} \times \dfrac{60\ \text{s}}{1\ \text{min}}}$$

$$I = 0.025\ C \cdot s^{-}\ \text{or}\ 0.025\ \text{A}$$

Activities and Assessments:

1. A solution of a metal ion $M^{3+}_{(aq)}$ is electrolyzed by a current of 5.00 A. After 10.0 minutes, 1.19 g of the metal is plated out.
    a. How many coulombs are supplied by the battery?
    b. What is the identity of the metal?

2. A baby's spoon with an area of 6.25 square centimeter is plated with silver from silver nitrate using a current of 2.00 A for two hours and 25 minutes.
    a. If the current efficiency is 82.0%, how many grams of silver are plated?
    b. What is the thickness of the silver plate formed? The density of silver is 10.5 g/cm^3.

3. The passage of a current of 0.750 A for 25.0 min deposited 0.369 g of copper from a $CuSO_4$ solution. From this information, calculate the molar mass of copper.

LESSON 9: CHEMISTRY OF ENGINEERING MATERIALS
UNIT 1: The Molecular Picture of Materials

Introduction:

The inner picture of matter underlies in all the workable material utilized in problem solving. This module explores the realities of intermolecular structure guided by general chemistry principles such as the Kinetic Molecular Theory, phase changes and intermolecular forces. Material strength in particular was elaborated using these general chemistry principles. Other properties relating to the inner structure were excluded and are instead explored on the next modules focusing on the exploring commonly used Materials. This section serves as foundation as we later explore other specific Materials in the course.

Learning Objectives:

After successful completion of this module, you should be able to:

11.) Recognize the different utility of materials by their varying properties
12.) Deconstruct the Intermolecular Forces (IMF) involved in different phases of matter
13.) Utilize Phase Diagrams of pure substances and mixtures

Course Materials:

Assessment of Material Properties

Problem solving in the physical world all involves the clever use of matter in some sort. Matter around us when used in engineering are what we call Materials. Problem solvers select, shape and organize Materials into some final form of solution. Examples of which are everyday physical products, from our electronic personal devices, concrete homes, food and drugs – all of which are tools that provide for particular needs.

Assessing Material properties prior to planned usage is a problem to be planned in itself. The selection process for materials differ in each applied system; even the best material for a particular application can be inviable when used in another system. In the industry furthermore, it often happens that the material selected entirely depends on its availability and the budget constraints. Having a database and understanding of material properties is therefore crucial for servicing even the most unprecedented situations. Relevant material properties for the operation are identified, candidate samples are measured, and data is statistically treated when multiple test runs are possible.

This module aims to give a fundamental understanding of material properties as it arises from the molecular picture. It hopes to aid future material assessment by building on the basic principles learned in molecular chemistry and establishing its relation to material bulk properties.

Intermolecular Forces and the Strength of Materials

Materials possess different categorical properties such as chemical, optical, electronic, magnetic, and thermal properties. However, the engineering term “Strength of Materials” refers to properties related only to Mechanical Strength. To limit the scope of the module, only Mechanical Properties of Materials would be analyzed in this part. Mechanical Properties alone are numerous because, as previously emphasized, that a particular measured property always depends on the application.

Below is a brief discussion of some frequently measured Mechanical Properties of Materials. Their respective application area was also included to highlight their exclusive importance.

1.) Tensile Strength – Tensile stress is the stress state caused by an applied load that tends to elongate the material along the axis of the applied load, in other words, the stress caused by pulling the material. Tensile strength or ultimate tensile strength is a limit state of tensile stress that leads to tensile failure in the manner of ductile failure or brittle failure.

2.) Shear Strength – the resistance to the stress state caused by the combined energy of a pair of opposing forces acting along parallel lines of action through the material, in other words, the stress caused by faces of the material sliding relative to one another. An example is cutting paper with scissors or stresses due to torsional loading.

3.) Compressive Strength – the resistance to compressive stress which is caused by an applied load that acts to reduce the length of the material along the axis of the applied load, in other words, a resistance from squeezing the material.

4.) Elasticity – the ability of a material to return to its previous shape after stress is released.

5.) Hardness – a measure of the resistance to localized plastic deformation induced by either mechanical indentation or abrasion.

6.) Malleability – a material can be plastic deformed and shaped when cold. A malleable material can be plastic shaped with hammering or rolling without fracture.

7.) Plasticity – he ability of a solid material to undergo permanent deformation, a non-reversible change of shape in response to applied forces.

Within the plethora of Material Properties brings the question: “Where do these variations of properties come from?” This inquiry is settled by knowing the inner picture of the bulk material.
Materials are composed of Individual particles that can be classified by their chemical formula and polarity. The chemical formula can be short such as Metal Oxides in crystals (ex: Ruby [Al_2O_3], Amethyst [SiO_2]), or can be long chained such as high molecular weight synthetic polymers (ex: Polystyrene [C_8H_8]n, PVC [C_2H_3Cl]n). How these particles stack and interact influences the relaxation and inner structure of the material. Within molecules, these interactions are called Intermolecular Forces.

Molecules as composed by uneven electron densities can either be polar and non-polar. The interaction between the Polar and Non-Polar particles summarizes the following types of Intermolecular Forces:

1.) Ion-Dipole – are electrostatic interactions involving a partially charged dipole of one molecule and a fully charged ion.

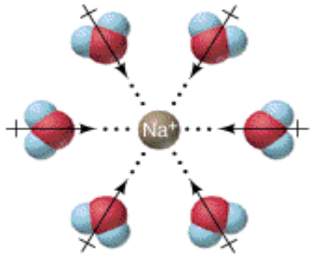
2.) Dipole-Dipole – are electrostatic interactions of permanent dipoles in molecules; which also includes hydrogen bonding.

3.) Hydrogen Bonding – An intermolecular attraction between a partially positively charged hydrogen in one molecule and a partially negatively charged oxygen, nitrogen, or fluorine in a nearby molecule.

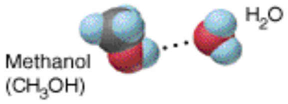
4.) Induced Dipole – a weak attraction that results when a polar molecule induces a dipole in an atom or in a nonpolar molecule by disturbing the arrangement of electrons in the nonpolar species.

5.) Dispersion Forces – forces caused by correlated movements of the electrons in interacting molecules, which are the weakest of intermolecular forces and are categorized as van der Waals forces.

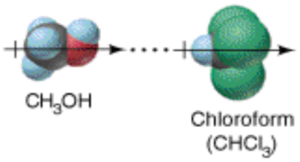
6.) Ionic Forces – The forces holding ions together in ionic solids are electrostatic forces. Opposite charges attract each other. These are the strongest intermolecular forces. Ionic forces hold many ions in a crystal lattice structure.



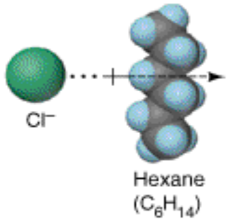
Ion-dipole



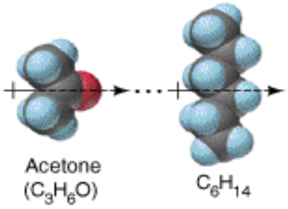
H bond



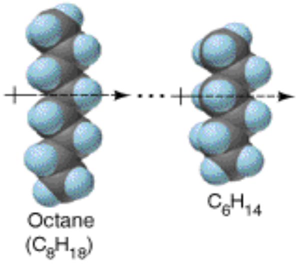
Dipole-dipole



Ion-induced dipole



Dipole-induced dipole



Dispersion

Intermolecular Forces present in a system depends on the polarity of the particles involved. Strong intermolecular Forces results in more proximal constituents – a denser configuration. Because Density is a measure of how intact matter is in its own volume, it is a direct contributor to strength. However, matter that is intact can become stronger by having an efficient internal stacking or structure.

A dense and ordered structure results into a material that could withstand more appropriate forces, while a dispersed and unordered structure could result in a weaker framework. For example, Crystals withstand compression because of their density and consistent ordered structure. Meanwhile Amorphous structures, which has a more random internal structure, cannot withstand compression. Glass and charcoal for example are amorphous and both can be too brittle.

Another major contributor to system stability is Molecular Weight. Low molecular weight substances such as water (18 g/n) is not a mechanically strong material in comparison to high molecular weight substances such as Polymers (40kg/n).

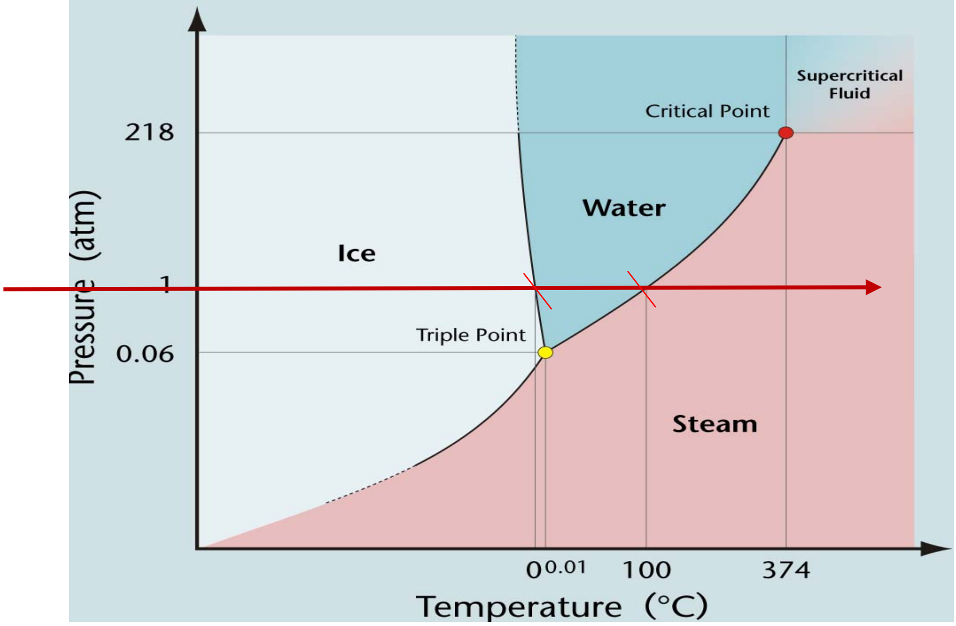
Molecular weight, Internal structure and Intermolecular Forces all play in part to the capacity of the material to be dense, stable and ordered. The appearance of substances observed as Phases, commonly solid, liquid, and gas, are some manifestations of this internal order.

In the final part, we review the Kinetic Molecular Theory and Phases Diagrams – tools that map all the possible internal orders of substances or mixtures.

A. The Phase Diagram Of Pure Substances And Mixtures

i.) Phase Diagram For Pure Substances

Water is one of the few substances which we have a daily interaction with all of its common Phases. Solid water is used to chill beverages and preserve perishable goods, Gaseous water is used as working fluid in steam engines and cooking, and Liquid water of course as a household utility. To transform water from a more kinetic phase to another, we add heat until it reaches the threshold temperature – following the kinetic molecular theory. At 100 Celsius water becomes steam, and at 0 Celsius it becomes ice.



These transformations can be better visualized using a guide known as the “Phase Diagram”. A discussion of this phase diagram (for pure water) is illustrated from the previous figure.

Notice that the diagram is a Pressure vs Temperature space. Certain regions feature a configuration of the molecules either as ice, water or steam. In the sea or ground level, an atmospheric pressure of 1 atm is experienced in our environment. Thus, using the y-axis of the graph, a line can be drawn through 1 atm of pressure parallel to the x-axis. Doing so, this line intersects the boundary between phases twice. One intersection is at the Ice-Water boundary, and the another on the water steam boundary. These intersections when projected down to the x-axis shows the known melting point (0 C) and boiling point (100 C) of water under the 1atm pressure of the environment.

In the instance of different environmental pressure, this temperature threshold changes with different y-values in the graph. On higher pressures, the water-steam boundary occurs on higher temperatures, while on lower pressure the boundary temperature is lowered; thus, making it easier to boil water.

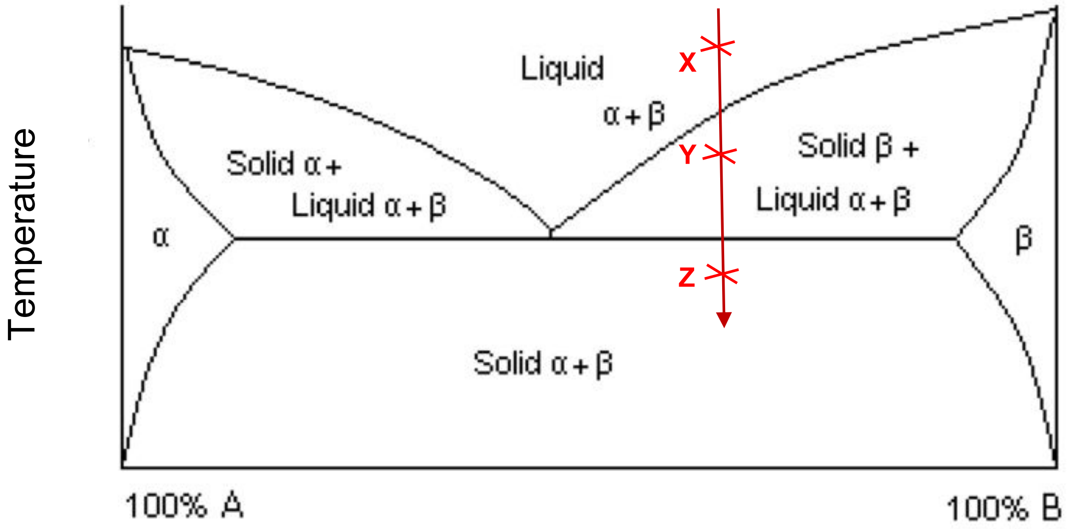
Furthermore, in the example P vs T phase diagram are two curious features that demands discussion: the “Triple Point” and the “Super Critical Fluid” region.

The triple point is a unique combination of Temperature and Pressure where all three phases are in equilibrium and won’t change phase regardless it is a solid, liquid or gas. For example, in a temperature and pressure combination that lies in the region of liquid water (say 1 atm and 25 Celsius), ice mixed with liquid water will subsequently melt in time. However, at the triple point (specifically 0.06 atm and 0.01 Celsius), ice would never melt in water regardless how long you leave it be.

On the other hand, the “Super Critical Fluid” is a Phase region occurring at both high temperature and pressure. Super critical fluids are considered as another configuration of water; having a combination of both liquid and gas properties. It is also termed as “heavy gas” because it has the same fluidity and permeating capability as steam, while also having the same density or “heaviness” as that of liquid water. This combination of fluidity and density makes supercritical fluids ideal for very efficient solute extraction processes such as removing caffeine from coffee beans.

ii.) Phase Diagram For Binary Mixtures

Phase diagrams display configuration regions of solid, liquid and gas commonly plotted in varying Pressure and Temperature. Though, another variation of the Phase Diagram is the Temperature vs Concentration plots which are constructed while handling the system pressure constant (mostly at 1 atm). This version of the phase diagram plot is used when analyzing the occurring phases within compatible mixtures. In binary mixtures, two chemicals interact to form a degree of compatible intermolecular arrangements. However, remember that each state has its boundary limits controlled not only by Temperature and Pressure, but also the concentration of individual components.

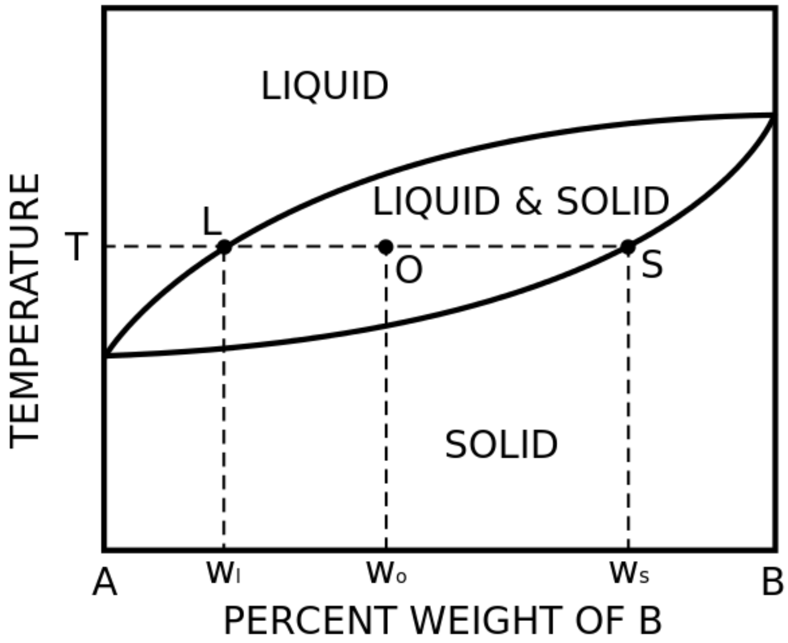


Take for example a mixture of water and chocolate powder: the compatibility of two mixtures often has a limit, or a “saturation”. At a given temperature, there is only an amount of chocolate powder that an amount of water could hold within the same phase. Any excess powder will definitely settle to its own phase (settle into its own solid phase) and will not be part of the water-chocolate powder colloid phase anymore. The binary phase diagram above further builds on the concept of saturation.

Starting from point X, lowering the system temperature down to points Y or Z shows how solid phases develop in liquid mixtures. Point X lies in the monophasic region where both alpha and beta components are liquid. Lowering the temperature to point Y yields a two-phase region where solid beta crystallizes from the previously exclusive liquid state. The component that crystallize into solid depends on which component is more concentrated and this can be expected from the mirrored Y area to the left. Lastly, lowering the system temperature further to point Z accesses another monophasic region where both components are again mixed compatibly both in their solid state.

The areas on the sides which are not discussed on the XYZ process line occurs at the extreme imbalance of the mixture composition. These are areas of mostly pure composition and is a solid phase mixture dominated by one component. These extreme areas show how important concentration is in phase equilibria for it can affect the permissible phases between components you intend to mix.

iii.) The Lever Rule For Binary Mixture Concentration



Knowing the concentrations in the two-phase area of binary phase diagrams is not that straightforward. One must understand that the %weight read by projecting your system point to the x-axis is the overall %Weight of B. However, that value does not directly tell how much liquid or solid is in the mixture nor would it directly show how much B is distributed between the mixed liquid and the solid phases.

We use the **point O** in the graph to elucidate this crucial account. Projecting point O to its corresponding x-axis value gives **Wo**, which is the ***overall percent weight of B in system O***. However, point O is in a binary phase region, meaning that the component B is distributed in the liquid-solid colloidal phase. The component B then in Wo is distributed in two phases.

To know the distribution of B between the solid and liquid in O, an isothermal line is constructed known as the **"Tie-Line."** This is a line segment passing through the system temperature T, intersecting the liquid and solid saturation lines at points L and S respectively. Projecting point L to the x-axis gives **Wl**, ***the concentration of B in the liquid phase***. Doing the same for point S gives **Ws*****, the concentration of B in the solid phase***.

So far knowing Ws and Wl gives the percent weight of B in the solid and liquid mixture. Yet, we still don't know how much liquid mass (**ml**) and how much solid mass (**ms**) is in the point O mixture. These weights can be known by utilizing the **"Lever Rule"** which computes for **%ml** and **%ms** of the total mass (**m**) of the O binary system.

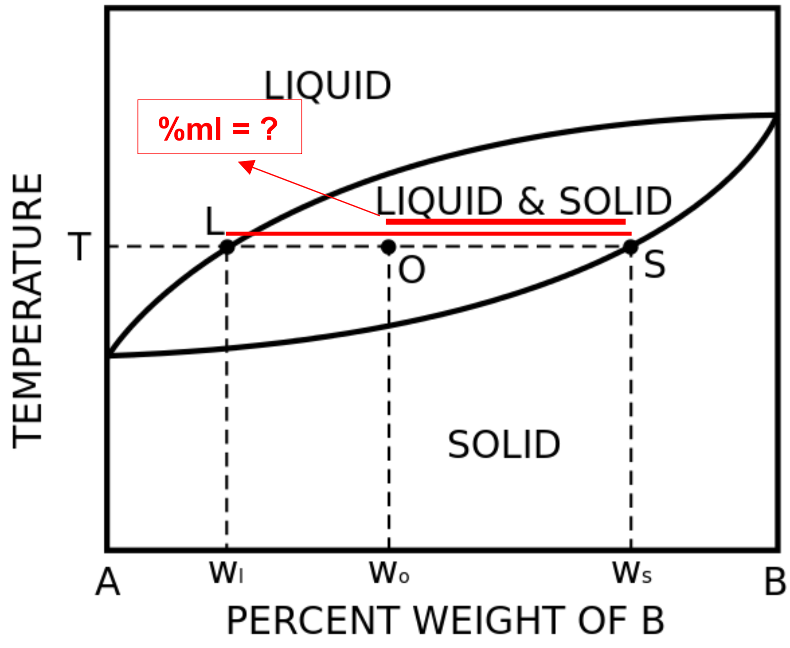
Total mass of system O = **m** = **ml** + **ms =** Mass of liquid and Solid

where: ml = m x (**%ml**)
ms = m x (**%ms**)

The “Lever Rule” can be easier utilized by breaking the tie line into three line segments: **OL**, **SO** and their total **SL**.

where:
OL = Wo – Wl
SO = Ws – Wo
SL = Ws - Wl

To know the percent mass of liquid (%ml) in system O, we divide the segment OS by the segment LS. Notice that OS is the segment closer to the solid side of the diagram, thus it is called a “lever” because the numerator used seems to be in the opposite side of the %m that you want to know.



%ml = **SO** / **SL**
%ml = (**Ws – Wo**)/(**Ws – Wl**)

Or visually:

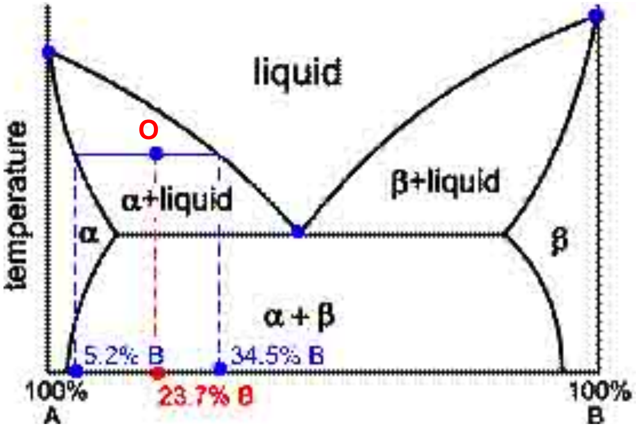
%ml = **SO**

Divided by the segment

SL

The percent solid (%ms) in our binary phase system O can be computed similarly by dividing the opposite line segment SO with the main line segment SL. Realize that the tie line is only used for points occurring on binary phase regions. If a point occurs on a one-phase area (such as exclusive solid and liquid areas), Wo is enough to describe the distribution of B in that singular phase.

SAMPLE PROBLEM: Calculation of %ml and %ms on a Two-Phase point in the Phase Diagram.



Answer the following questions using the phase diagram above given that the system is at the point O in the graph which weighs 150g.

1.) How many phases are in point O and what are they? (Ans: 2 phases, alpha and liquid.)
2.) How much of the total weight B is with the alpha phase? How much of A is in alpha phase? (Ans: 5.2%B of the total weight, is mixed with the mostly A at 94.8%).
3.) How much of the total weight B is with the liquid phase? How much of A is in liquid phase? (Ans: 34.5%B and 65.5%A.)
4.) How much of the total 150g is liquid? How much of the total 150g is alpha?
    Ans: i.) First get the %m(alpha) and %m(liquid) using lever rule and taking note of the "opposite" segments.
        %m(alpha) = 100*(34.5-23.7)/(34.5-5.2) = 36.86%
        %m(liquid) = 100*(23.7-5.2)/(34.5-5.2) = 65.1
        ii.) Multiply the total weight of O with the percentages.
        Mass of Alpha = %m(alpha)*150g/100 = 55.29g
        Mass of liquid = %m(liquid) *150g/100 = 94.71g

Activities/Assessments:

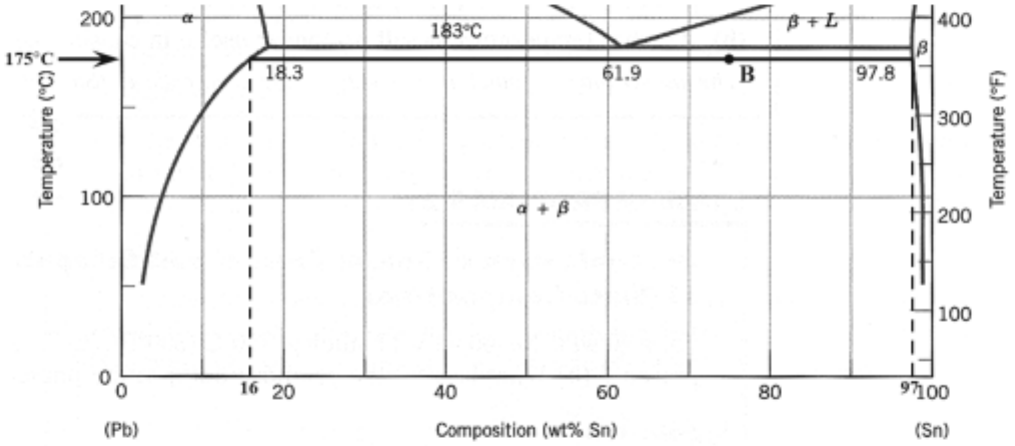
6. Find five other Material Properties not discussed in this module and relate these to the Molecular Picture of some related materials. What industry does the measure of this property useful for? Furthermore, classify whether it is Intrinsic or extrinsic, and whether it is Chemical, Physical or of another category.

7. Illustrate how the Intermolecular Forces could differ from being Solid, Liquid, and Gas? Which of the discussed Intermolecular forces does each of these matter states are usually dependent?

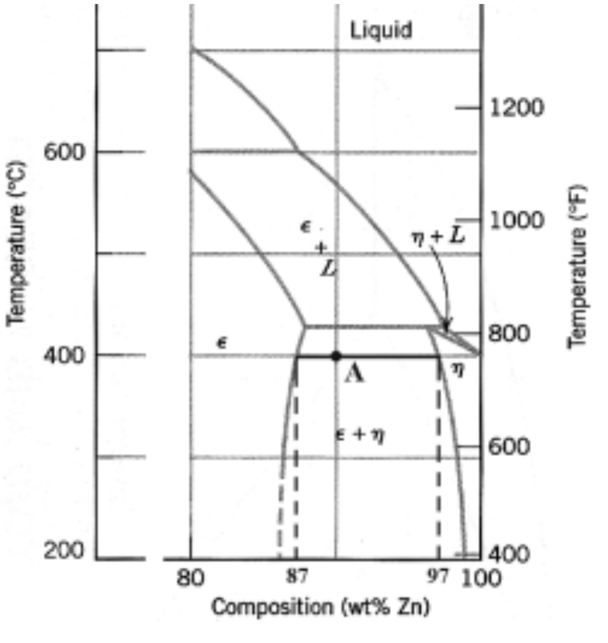
8. Research the Eutectic point that is present in phase diagrams. How will you explain its importance using the concept of equilibria? How is it expressed in Equilibrium Constant?

For 4 and 5, Solve for the weights of the phases for the following system points on the phase diagrams:

9. Given that the system is 500g in total, how is this distributed to the alpha and beta phase?



10. Given that the system is 750 in total, how is this distributed to the ε and η phase?



LESSON 9: CHEMISTRY OF ENGINEERING MATERIALS
UNIT 2: Simple Atomic Crystal Structures

Introduction:

Moving from individual atoms and molecules, the way these particles stack pertains to an inner structure that has effects on material strength and properties. The kinetic molecular theory revisited last module shows that as the molecules become more kinetic, the phase of matter gets increasingly fluid. We will focus on solid materials this chapter which are matter on their lower kinetic states. Low kinetic particles allow ordered arrangements and consistent molecular structures which greatly affects the strength of a material. This module will focus on highly ordered internal structures which are termed Crystals. We will use the consistent structures in Crystals in order to apply geometrical concepts in computing Densities and Ionic radii of crystal atoms. This module also introduce the concept of Crystal Diffraction which shows how the wave nature of light interacts within the atomic spacings inside the ordered structure of crystals.

Learning Objectives:

After successful completion of this module, you should be able to:

1.) Differentiate apparent bulk characteristics of amorphous and crystalline structures.
2.) Describe the types of crystal lattices and apply geometry in their dimensional character.
3.) Compute material density using unit cell geometry and formula weights.
4.) Demonstrate understanding of basic crystal diffraction utilizing Bragg's Law.

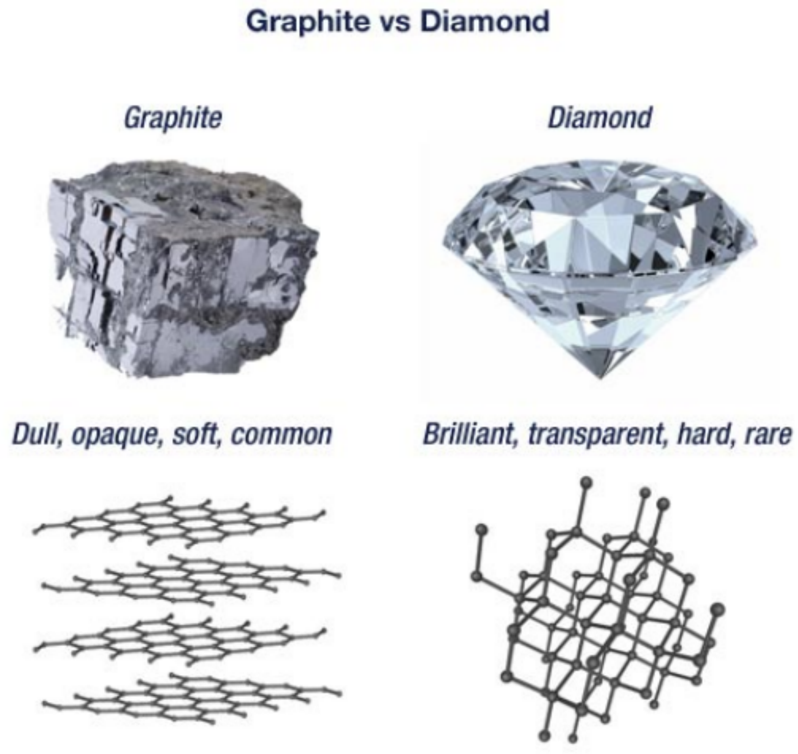
Course Materials:

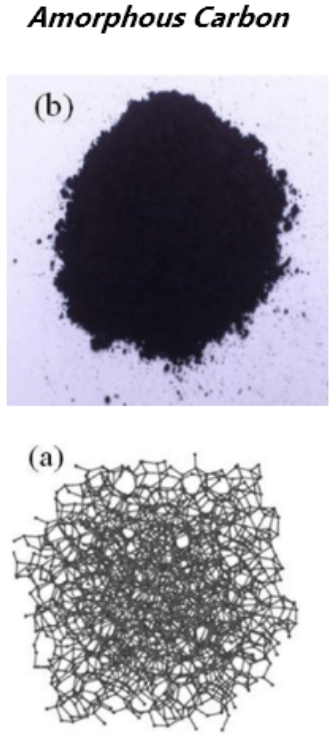
Bulk Character of Crystalline And Amorphous Solid Material Structures

Last module we established the intermolecular forces present between polar and non-polar particles. The strength of available forces is apparent on the material's phase: with solids having the strongest intermolecular forces, while gas have only weak forces in comparison. This chapter focus on the Solid phase, which is the most usual form of material used at room temperature.

Room temperature Solids are known to be typically dense materials, in comparison to gas and liquids, because of their higher molecular weight. Water for example is a very light and small molecule with only 2 hydrogens and 1 oxygen weighing 18g per mole in total. Thus, water is not solid in room temperature. In contrast, Polymers weigh around 40 kg per mole, and unlike water is composed of long intertwined chains of linked monomers. These longer chains of atoms are immobile unlike the energetic small particles of water. The tendency for these heavy and long particles is to sediment or coagulate to a solid phase. However, lighter chemicals can be expected to be solid if it possesses strong molecular forces, like the ion-ion intermolecular forces in NaCl for example which is a stable solid in room condition.

This module will discuss the effects of Intermolecular Structure in Material Strength, which is also a function of the intermolecular forces. A solid can either be Amorphous or Crystalline, depending on its internal regularity of structure. Amorphous solids are randomly oriented and lack internal regularity. In contrast, Crystalline solids contains internal repeating patterns much like wall papers with a repeating design. This regularity in Crystals allows for a systematic description that could be understood using geometry. Ice is an example of an Amorphous solid, while Table salt is an example of a crystal. Their internal differences could be confirmed when shattering big blocks of the material. Salt will shatter into smaller cube like shapes preserving its internal geometry: the fracture angles are of accordance with the angles in a cube. Meanwhile, ice will shatter into random pieces since its internal fracture points are random, showing it has no internal regularity. Polymers on the other hand can be Amorphous or semi-crystalline. Because of their high molecular weight and longer length, it is harder for polymers to achieve perfect internal geometry. However, the bulk result of these long-intertwined polymers does not lack strength. Polymers like polyethylene (PET) and polypropylene (PP) are household and industry materials that are frequently used because of their strength and machinability.





A good display on how internal structure is related to material strength is to examine the behavior of different pure solid carbon allotropes. Diamond, Graphite and Coal are all allotropes of carbon-only compounds with connected C-C covalent bonds. Yet their utility, strength, and appearance all differ just because of their different internal structures.

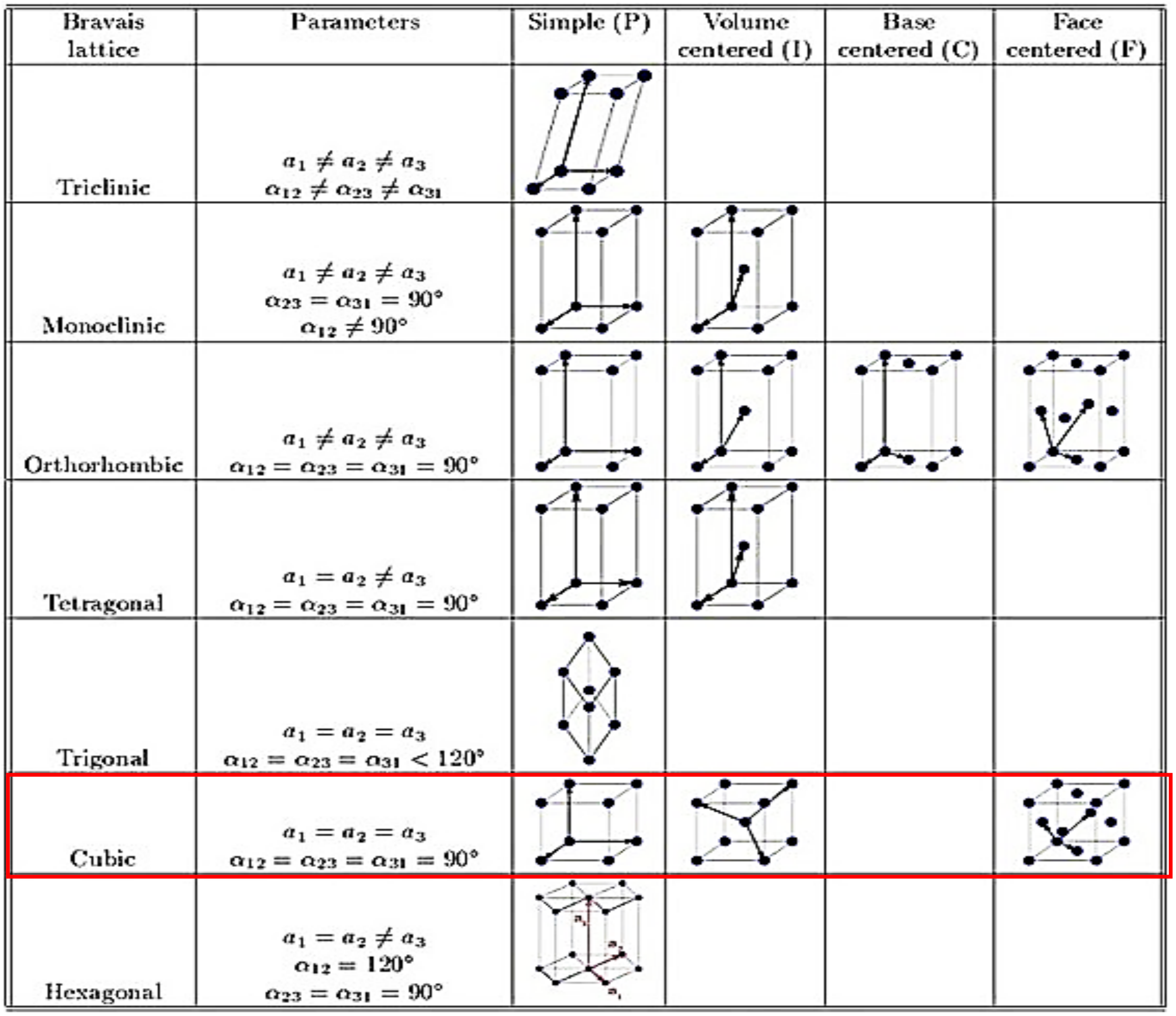
The figure above shows how coal, a brittle, combustible material is a carbon allotrope in its amorphous form. This brittleness was caused by a non-ordered internal structure with carbon to carbon bonds not reinforcing each other. A force applied on this amorphous coal structure is not distributed to the whole material, and therefore no force cushioning occurs, allowing the material to easily break at the point of force contact.

Graphite has an ordered 2-d crystal structure but it is not a 3-d crystal. Each 2-d graphite sheet can easily slide with each other – making small graphene flakes contained in pencil lead easily slide and mark on paper. However, a long single sheet of graphene is actually a very strong material. A wide square of graphene sheet, that is one-atom thick, is about 200 times stronger than steel while being 6 times lighter and 20-25% elastic.

Lastly, Diamonds are a 3-d crystal of tetrahedral patterned carbon. Diamonds are known as one of the hardest materials available, and this is because of the repeating tetrahedral pattern of their C-C covalent bonds. Unlike on amorphous coal, applying a point-force on diamond will be efficiently redistributed to the whole material because of their internal structural reinforcement. This inherent hardness makes diamond an ideal material for specialized industrial work such as drilling for oil wells.

Notice also that each carbon allotrope behaves differently with light. Amorphous substances are often black bodies that could absorb but not reflect light because of the irregular and heavy mesh of its internal structure. This heavy mesh of high molecular weight strings cannot facilitate proper light diffraction because the angles where light could bounce are internally random. Lighter and thinner amorphous solid substances like thin PET bottles and glass could transmit light only because of the larger interstitial distances between their atoms. However, thicker amorphous materials would make it opaque. The regular order in crystal structures on the other hand makes it possible to diffract light at consistent angles. Later we will explain this light interaction further and then quantify it utilizing Bragg’s Law.

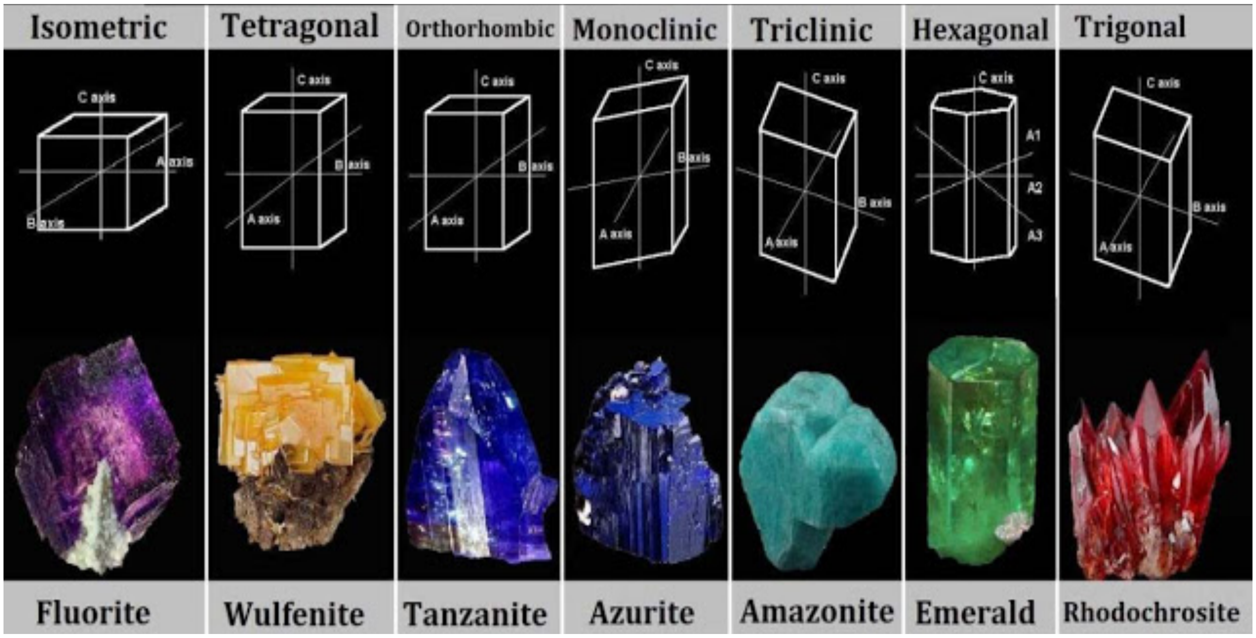
Crystal Lattices



Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

In the previous table, analyze the segments and angles as they differ and relate to each other. Amorphous substances do not have a basic geometrical structure, but Crystals could be classified using the geometries available above.

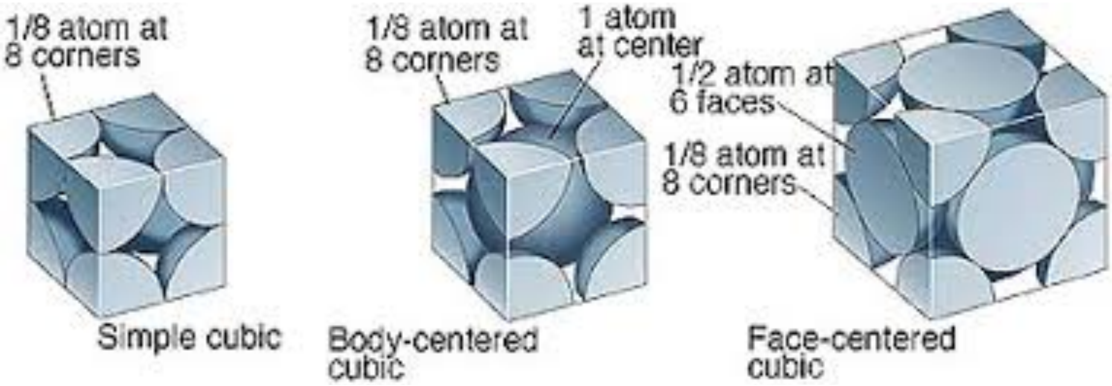
Bravais Lattices categorize the geometry in ordered crystals with angular and segmental parameters. There are certain patterns of equal and unequal segments, 90 degree and non-perpendicular inner angles, and centered and face/base centered arrangements. The dots represent the location of a particle or molecule, but the volume is considered to bisect the molecules into segments that occupy the isolated space. The isolated molecular pattern by the shape volume are what we call Unit Cells. Unit Cells are repeated patterns that are uniform to the whole crystal matrix. Each type of lattice differs and if two of the same substance utilize different lattices, they are considered to be of a different solid phase. Different solid phases further subdivide the solid region in phase diagrams, which are labeled with Greek letters (such as alpha and beta) to identify that they are different internal rearrangement of the substance.



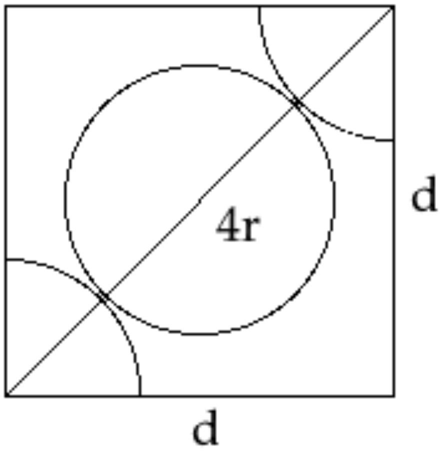
Gemstones that beautifully adorned jewelry can be found in nature in certain jagged shapes. Upon inspection, the angles in these shapes corresponds to the Bravais lattices. The gemstones are easier to cut in the angles where the lattice could preserve itself. These angles occur on the planes that are parallel to zones of weak bonding within the crystalline substance. In calcite for example, the crystals break along 3 planes of weakness within the crystal structure, forming rhombohedral blocks. These mineral cleavage planes are always at the same angles: in 3 directions, and the x, y and z dimensional axes.

Knowing possible crystal structures of a material could be used alongside its chemistry. For example, one could deduce what its internal structure just from the bulk material density. The periodic table gives us a method for computing formula weights and ionic radius, and when combined with the internal structure geometry would let us deduce impurities inculcated within the investigated crystal. For computation simplicity, the next section will only sample some of these calculations using Cubic crystal structure variants; namely, the primitive cubic structure, the Body Centered Cubic structure (BCC), and the Face Centered Cubic structures (FCC). Furthermore, since complex molecules have different geometries, our computations will only involve spherical atoms embedded in the lattice so we could utilize its radius.

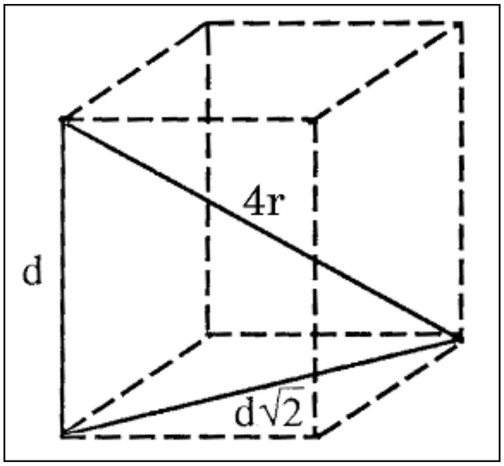
Cubic Structures are both equilateral and equiangular, making it the simplest system to apply trigonometry. Refer to the figure below shows how particles are subdivided to fit in the cube volume.



As shown above, there are a total of 8 corners that have 1/8 parts of atoms in a simple cubic structure for a total of 1 atom (8 x (1/8)). In BCC, there is an additional full atom at the center making a total of 2 atoms. Lastly in FCC, there is an additional 1/2 atom on each cube face for a total of 4 atoms.



FCC structure



BCC structure

Aside from the total number of atoms in the cube, the cube dimensions as a function of the radius should be established for the three cubic structures. The side of the cube is important because its volume is a simple cube (x^3) function of it. The simple cubic has 2 atomic radii on its side, but for the FCC and BCC, the illustrations above establish the side (d) as a function of the atomic radius (r). Pythagorean theorem was used to derive these functions.

Physical Properties From Unit Cell Geometry

I.) PROBLEM TYPE#1: Calculation of Ionic Radius

Palladium crystallizes in a face-centered cubic unit cell. Its density is 12.023 g/cm3. Calculate the atomic radius of palladium.

1) Calculate the average mass of one atom of Pd:

$106.42\ \text{g mol}^{-1} \div 6.022 \times 10^{23}\ \text{atoms mol}^{-1} = 1.767187 \times 10^{-22}\ \text{g/atom}$

2) Calculate the mass of the 4 palladium atoms in the face-centered cubic unit cell:
1.767187×10^{-22} g/atom times 4 atoms/unit cell = 7.068748×10^{-22} g/unit cell
3) Use density to get the volume of the unit cell:
7.068748×10^{-22} g ÷ 12.023 g/cm^3 = $5.8793545 \times 10^{-23}$ cm^3
4) Determine the edge length of the unit cell:
$5.8793545 \times 10^{-23}$ cm^{3}3 = 3.88845×10^{-8} cm
5) Determine the atomic radius:
r = d ÷ 2(√2) <--- an alternate formulation
r = 1.3748×10^{-8} cm

II.) PROBLEM TYPE#2: Calculation of Material Density

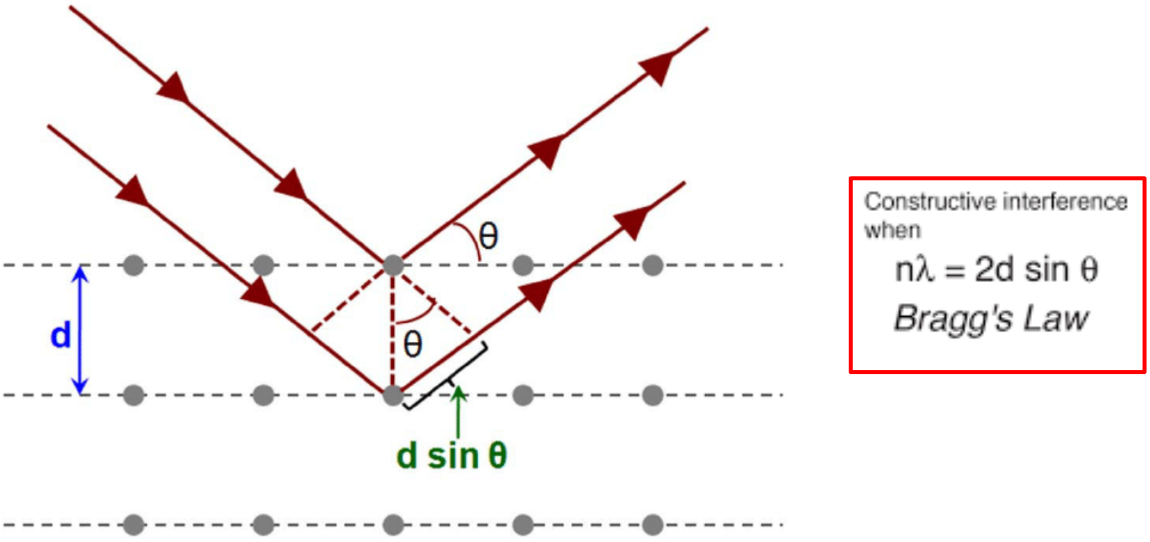
The unit cell of platinum has a length of 392.0 pm along each side. Use this length (and the fact that Pt has a face-centered unit cell) to calculate the density of platinum metal in kg/m^3

1) Calculate the volume of the unit cell in meters cubed:
392.0 pm times (1 m / 10^{12} pm) = 392.0×10^{-12} m = 3.920×10^{-10} m
$(3.920 \times 10^{-10}\ \text{m})^3 = 6.0236288 \times 10^{-29}$ m^3
2) Calculate the mass of Pt in the unit cell in kg:
195.078 g/mol divided by 6.022×10^{23} mol^{-1} = 3.239422×10^{-22} g
3.239422×10^{-22} g times 4 = $1.2957688 \times 10^{-21}$ g
$1.2957688 \times 10^{-21}$ g times (1 kg / 1000 g) = $1.2957688 \times 10^{-24}$ kg
3) Calculate the density:
$1.2957688 \times 10^{-24}$ kg / $6.0236288 \times 10^{-29}$ m^3 = 21511 kg / m^3
The standard value is 21450 kg / m^3

III.) Light Interference In Crystals

Sitting in a lamped room, a sharp silhouette will be formed if you put your hand close to the wall. As you move your hand closer to the light source and farther away the wall, this silhouette will be smudged and fuzzy. This fuzziness is a sample of light diffracting around your hand. Diffraction is the bending of waves, electromagnetic waves in this case, as it encounters an obstacle or an aperture (refer to Huygens's Principle). Like wading your hand through water, the rays of lamp light spread inward your fingers as they pass by – thus smudging your shadow outline. All waves behave like this: pond water waves diffract around the edges of walls and sound waves curve out at the edges of the concert stage.

Another related principle, Interference, refers to the way these waves interact with each other. Positive interference occurs when waves add and form a larger wave, like the build-up of larger tidal waves. Negative interference on the other hand, occurs when waves cancel each other out. This could be best visualized with a string that is vibrated oppositely on its two ends. Once the opposite waves meet at middle of the string, their opposing amplitude would cancel each other out and the wave will disappear at the center.



We could utilize this diffraction and interference phenomena of electromagnetic waves in analyzing small interatomic apertures, such as the spaces within crystals. In particular, X-rays are the spectrum region of choice in crystal diffraction techniques. X-rays have wavelengths comparable to the distances between the crystal atoms (d). Therefore, this sufficient space allows X-rays to pass through, which will then after diffract upon contact with an atom in the crystal lattice. Sir William Lawrence Bragg and his father demonstrated this crystal phenomena written formally as Bragg's Law: a formula that shows the condition of constructive interference required for diffracted x-rays. Referring to the figure and the formula above, Bragg's Law shows that if the phase lag [2*(d sin θ) where θ is the incident angle of the X-ray] between two x-rays is an integer (n) multiple of the wavelength (λ), the two waves would interfere constructively and combine their intensity. If the phase lag is not an integer of the wavelength, the two waves would interfere destructively and diminish or cancel each other out.

SAMPLE PROBLEM#1: Finding X-ray Wavelength for Crystal Diffraction

The spacing of one set of crystal planes in NaCl (table salt) is d = 0.282 nm. A monochromatic beam of X-rays produces a Bragg maximum when its glancing angle with these planes is θ = 7^{o}. Assuming that this is a first order maximum (n = 1), find the wavelength of the X-rays.

Ans:
The Bragg law is 2d sin θ = nλ
λ = 2d sin θ *(1/n) = 2 × (0.282 nm) × sin 7^{o} * (1/1) = 0.069 nm

SAMPLE PROBLEM#2: Finding Interatomic Distances through Braggs Law

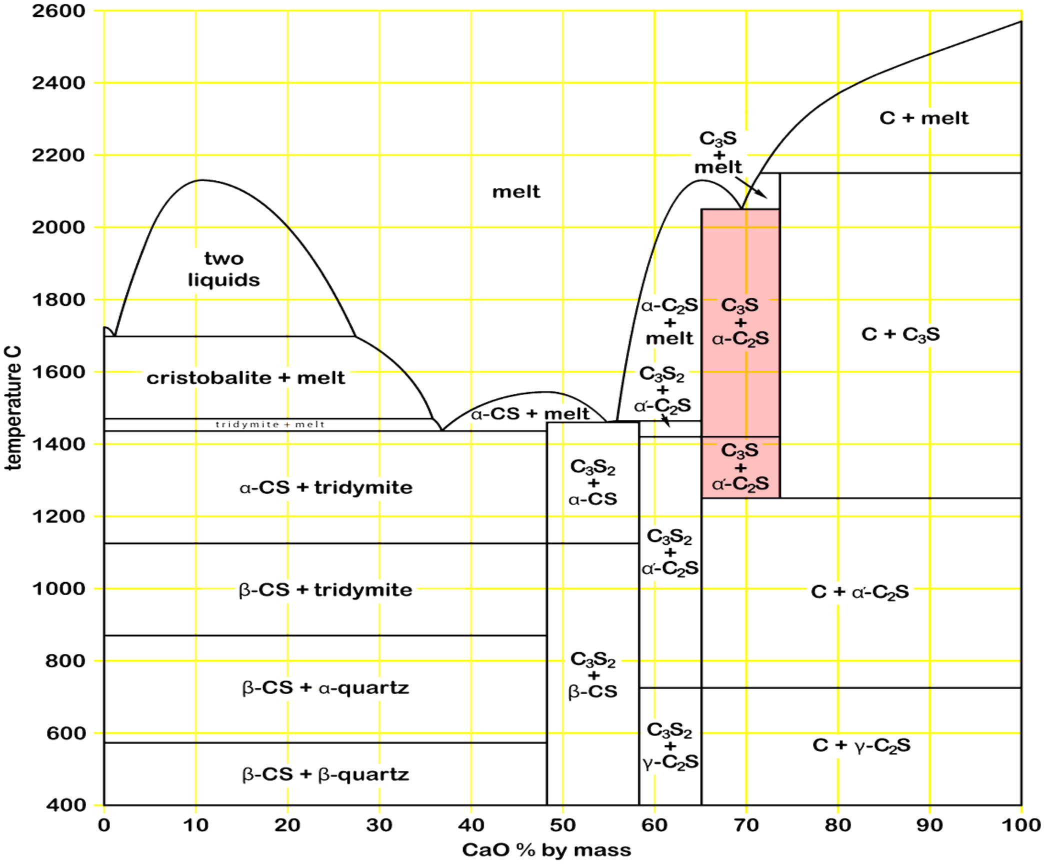
X rays of wavelength 0.154 nm are diffracted from a crystal at an angle of 14.17^{0}. Assuming that *n* = 1, what is the distance (in pm) between layers in the crystal?

Ans:
λ = 2d sin θ *(1/n)
d = λn / (2d sin θ) = 1 x 154 pm / (2 x sin 14.17) = 314.54 pm

Activities and Assessments:

1.) Research five mineral gemstones and find their chemical composition and crystal structure.

2.) Research the crystal structures in the following phase diagram for cement. How does each different crystal affect the strength of concrete? What does other small additives do to improve cement performance?



3.) A crystal with spacing between planes equal to 0.394 nm diffracts X-rays with a wavelength of 0.147 nm. What is the angle for the first order diffraction?

4.) In a diffractometer, X-rays with a wavelength of 0.1315 nm were used to produce a diffraction pattern for copper. The first order diffraction (n = 1) occurred at an angle θ = 25.25°. Determine the spacing between the diffracting planes in copper.

5.) The edge length of the unit cell of LiCl (NaCl-like structure, FCC) is 0.514 nm or 5.14 Å. Assuming that the lithium ion is small enough so that the chloride ions are in contact, calculate the ionic radius for the chloride ion.

6.) Calculate the density of gold, which has a face-centered cubic unit cell with an edge length of 407.8 pm.

LESSON 9: CHEMISTRY OF ENGINEERING MATERIALS
UNIT 3: Typical Solid State Materials

Introduction:

This module presents the structure of the most common materials used in the 20th century. Using our previous discussion of kinetic molecular theory, phases, amorphous substances and crystals, we will see more specific examples of how these concepts apply on Metals, Semiconductors, Polymers, Composites and Nanomaterials. The structure of these materials was explored and related to why these materials behave as used in their specific applications. The studies on these materials are broad and different, for they are specific industries among themselves. This module serves as a theoretical introduction discussing the working theories utilized by the specialized industries working with these materials.

Learning Objectives:

After successful Completion of this module, you should be able to:

1.) Demonstrate understanding of the electronic properties in metals and semiconductors through the Band Theory.
2.) Visualize the macromolecule of polymers and compute their molecular weights.
3.) Explain the effects of internal structure in composites and nanomaterials.

Course Materials:

Metals and Semiconductors

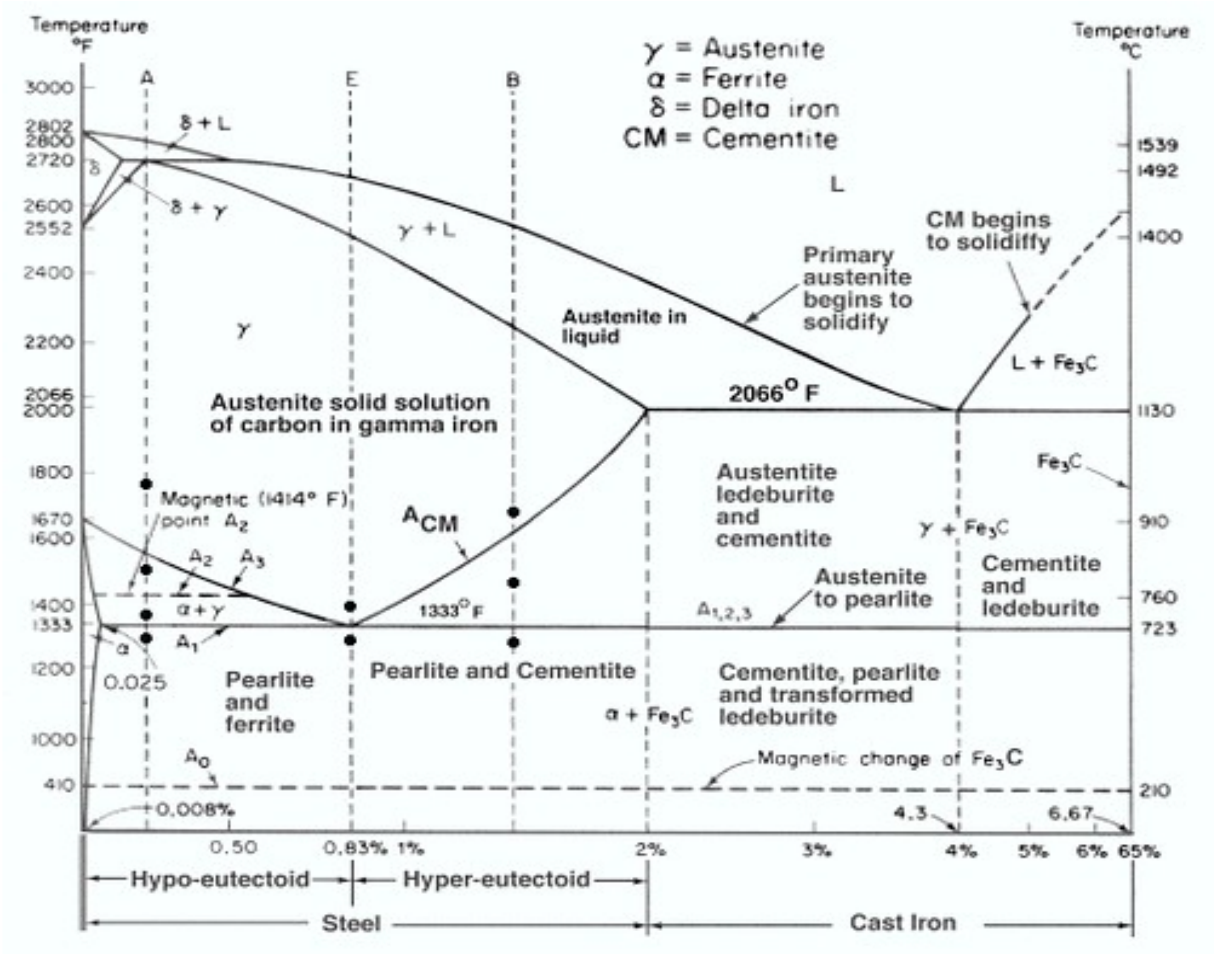
Copper Wires, Steel Reinforcements, Gold Plating, Aluminum Cans, Bronze Coins, Lead Shields – Metals are the Material Workhorse of Industry. Studying Metals would be the essential to Material Science because of its prevalent industrial applications alongside its atomic simplicity. Unlike long intertwined chains of Molecules, Metals are easier to mathematically model since the Metal matrix is demonstrated simply as adjacent metal atom spheres. Therefore, we could apply our simplified arithmetic of unit Cell geometry as discussed in the previous module. Furthermore Alloys, which are one of the important and prevalent industrial use of Metals, are considered as physical mixtures. And as such we could also apply what we have learned on binary phase diagrams and use it to compute each individual concentration. However, since metals are often utilized in the solid-solid phase, knowing the individual concentrations in the phase diagram is rather straightforward.

We would also introduce the “Band theory” which is a quantum mechanical model related to the electrical properties of metals. This theory is essential in explaining Semiconductors, which alongside with metals are two of the most essential materials in the electronics industry. In these discussions we will see that another group of elements, the Metalloids, are often mixed with trace Metals in order to fine tune their electronic properties as required by the increasingly precise electronic components.

A. Homogenous Solid Solutions: Metal Alloys

Alloys are used in a wide variety of applications, from the steel alloys, used in everything from buildings to automobiles to surgical tools, to exotic titanium-alloys used in the aerospace industry, to beryllium-copper alloys for non-sparking tools. They are made from the high-temperature molten state mixing of metals, such as combining gold and copper produces red gold, gold and silver becomes white gold, and silver combined with copper produces sterling silver. Some Alloys are also Metals combined with one or more other non-metallic elements. For example, Iron combined with non-metallic Carbon or Silicon, produces alloys called steel or silicon steel. These Metals are alloyed so that its strength, hardness and other properties could be altered, enhanced, and even as a way to reduce their costs.

Note that Alloys are only combined with low quantities of Non-Metals, and that alloys are supposed to be more metal-like in character. Substances such as aluminum oxide (sapphire), beryllium aluminum silicate (emerald) or sodium chloride (salt) are not alloys. These substances do not retain any of their previous metallic properties, such as electrical conductivity, ductility, opaqueness, and luster.



The above figure is a temperature vs concentration phase diagram for Iron mixed with small amounts of Carbon (.008 to 6.5%). Each Greek symbol represents a particular crystal structure of Iron (alpha, beta and gamma) while cementite (CM) is a hard but brittle ionic compound Fe3C. As we have learned previously, the concentrations of Iron could be deduced from this figure, directly if the mixture is entirely a solid solution, and using a “tie-line” if the mixture contains both liquid and solid parts.

This particular phase diagram is important for the production of Carbon Steel, which is segregated into three main categories: Low carbon steel (sometimes known as mild steel); Medium carbon steel; and High carbon steel. Mainly depending on Machinability, a specific range of carbon content is desired.

Low Carbon Steel which contain 0.04% to 0.30% carbon content, covers a great diversity of shapes; from Flat Sheets to Structural Beams. Because of the almost pure Iron content, it retained its metallic malleability. Other elements are also added or increased depending on the desired properties needed, for example: Drawing Quality (DQ) – The carbon level is kept low and Aluminum is added, and for Structural Steel the carbon level is higher and the manganese content is increased.

Medium Carbon Steel: Typically has a carbon range of 0.31% to 0.60%, and a manganese content ranging from .060% to 1.65%. This product is stronger than low carbon steel, and it is more difficult to form, weld and cut. Medium carbon steels are quite often hardened and tempered using heat treatment.

High Carbon Steel: Commonly known as “carbon tool steel” it typically has a carbon range between 0.61% and 1.50%. High carbon steel is very difficult to cut, bend and weld. Once heat treated it becomes extremely hard and brittle.

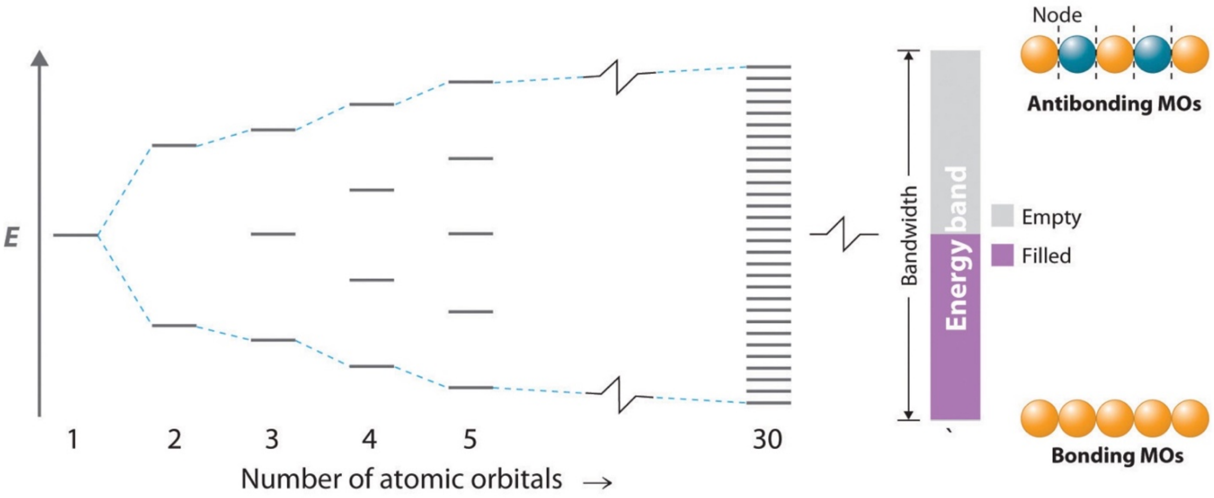
B. Electronic Picture of Metal Crystals

Metals are very interesting to discuss when it comes to how they interact with each other as they challenge our rudimentary knowledge about atomic bonding. Metals and Non-Metals form ionic bonds via transferring electrons and utilizing electrostatic action thereafter, forming “salts” such as NaCl or $CaCO_3$. While Non-Metal and Non-Metals share electrons and covalently bond to form molecular compounds like water H_2O or CO_2. But curiously, do Metals bond with Metals? As we have seen with Alloys, does mixing the different Metals make them react to form some sort of a unique compound?

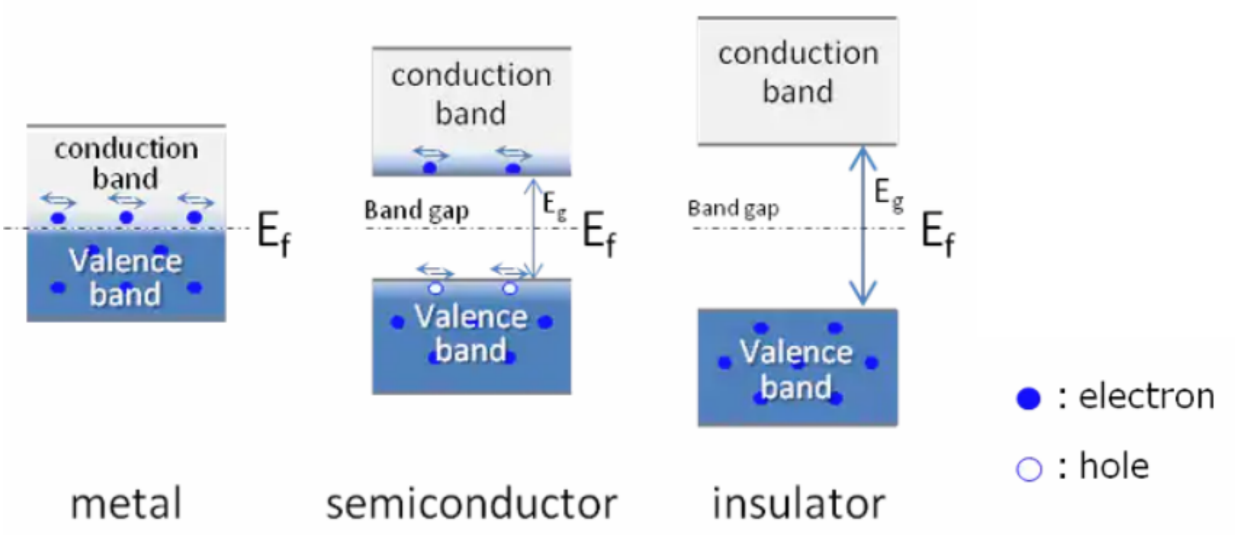
The answer is no; the Alloys are just mixtures that could be physically separated with heat and density without chemical reactions. Unlike ionic compounds and covalent compounds, Metals will not form localized electron regions such as what we see on the individual ions of ionic compounds or in the individual molecules with localized electron sharing between covalent bonded atoms. Instead, Metals form a “band” of valence electrons shared within the whole matrix of the material. This is what make Metals behave as good conductors. Because of their electron abundance (relative to their nuclear charge), these electrons could easily flow through the material when the proper voltage is applied. Understanding this “Band Theory” will help explain the interaction between metal atoms and its electronic properties. Band Theory uses concepts from the alternate bonding scheme of the Molecular Orbital (MO) theory and the quantum mechanical picture of the atom, so we would start the band theory discussion by revisiting some of these concepts.

The formation of both ionic and covalent compounds can be simply explained by the traditional Valence Bond theory; where Valence electrons are being transferred or shared. However, this model of bonding is insufficient in describing the concept of “delocalized” electrons, meaning electrons that do not stay on the same nuclei. Here we are aided by the MO theory that help describe the quantum picture of electrons when cooperating with each other. In quantum mechanics, electrons are modeled as a probability density or a “cloud” where an electron is thought to exist all of the same time, albeit on different percentages. Electrons also have the curious property of “spin” – where electrons could pair despite the same negative charge that should repel, as long as they have opposite spin value.

The MO theory depicts the allowed energy states these interacting electrons could occupy. These two states are the bonding and the antibonding state; or a state of attraction or repulsion between the electron clouds. These states are quantized energy levels, that is no in between values of energies are allowed except that of the bonding and antibonding energy levels. The lower energy is the bonding state, where the electrons have more stable positions because they are opposite spin paired, while the more energetic state is the antibonding state where the electron cloud densities are repelling due to having the same spins. We will now use these concepts to illustrate how an “electron band” forms using the figure below.



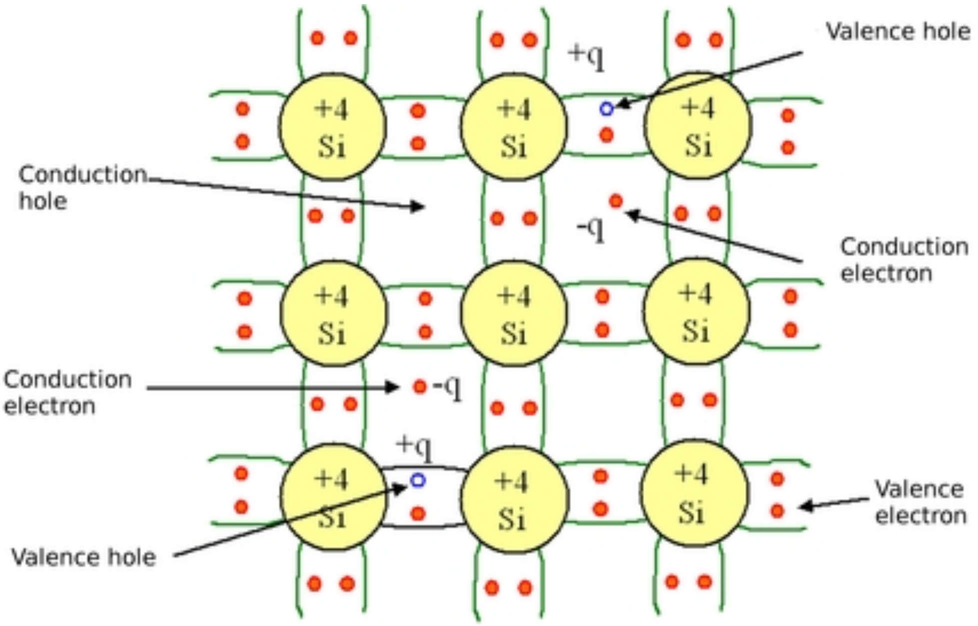
Same types of Metal atom have the same Valence electrons with the same energies. These high energy valence electrons are on position to interact with another neighboring valence electrons. Two electrons interact and form specifically one anti-bonding and one bonding orbital which is consistent with the MO theory of electron-to-orbital conservation. As the number of these interacting valence electrons increase, such as in a metal crystal, the generated orbitals aggregate to form a “band” or a range of energies that of similar in nature. The aggregate of bonding MOs with low energy, more stable, orbitals is the “Valence Band” or is the state where these valence electrons rests within its parent nuclei. When additional energy is applied such as an outside voltage difference, the electrons could be promoted to the higher energy anti-bonding MOs - the “Conduction Band” – which makes conduction possible, as electrons move through the charge difference provided.



On the figure above we see the different “band gaps” for different materials, which is the energy difference between the conduction band and the resting valence band. For metals, the band gap actually overlaps, meaning that the valence electrons could be conducted seamlessly without resistance. Insulators on the other hand have a relatively large band gap (around 9eV or more), meaning that an external voltage is required just to make electrons flow through the material. This gap is engineered and regulated. For materials we know as Semiconductors, a small band gap is engineered around 1 to 4 eV. We will discuss how the semiconductor works further on the next section.

C. Doping and Semiconductors

Electrical conduction is the result of electron motion within each band. When an electric field is applied to the material, electrons start to move in the direction opposed to its direction. An electron can move provided that it can find some free space elsewhere, and once an electron is promoted, it also leaves a free space behind (refer to the diagram below). This free space is called a “hole” (or valence hole) which is another available site within the energy bands that an electron can occupy. A material without these spaces, with fully occupied or empty energy bands, behaves as an insulator; because there is nothing to facilitate electron movement.



There are two ways on how we could manufacture this “hole” that facilitate further electron movement. One is to check whether the operating temperature allows such. This is the case for natural conductors with overlapping conduction and valence bands at room or operating temperature. However, for Insulators with gap energies exceeding ~9eV, the thermal energy on operating temperatures are insufficient to allow valence band electrons to leave their parent nuclei and be promoted to the conduction band. Semiconductors also work like insulators at these very low temperatures or 0 Kelvin. However, since the semiconductor energy gap (1eV to 4eV) is lower compared to insulators (9eV or more), the valence band is just slightly depopulated at room temperature (has minimal holes), whereas the conduction band is just slightly populated with electrons. This makes electrical conductivity for semiconductors very small at room temperature.

Another way to manufacture band holes and electron promotion is through Doping. Doping introduce impurities to an otherwise pure elemental crystal. This categorizes semiconductors into two basic types according to purity: Intrinsic and Extrinsic. Intrinsic semiconductors are pure substances with a natural 1eV to 4eV band gaps. Extrinsic semiconductors have artificial band gaps coming from the impurities through doping, which in effect, introduce valence electrons or holes to the crystal matrix. The impurity introduced in Extrinsic Semiconductors enables us to deeply modify its electrical properties, making it adjustable for more specific electronic applications such diodes, transistors, or optoelectronic applications such as light emitters and detectors.

Furthermore, Semiconductors are also classified on either a P-type or a N-type. A P-type semiconductor is an intrinsic semiconductor (like Si) in which an impurity acting as an acceptor (like e.g. boron B in Si) has been intentionally added. These impurities are called acceptors since once they are inserted in the crystalline lattice, they lack one or several electrons to realize a full bonding with the rest of the crystal. P-type semiconductors has a lower electron density n and a higher hole density p than the same intrinsic semiconductor. Electrons are said to be the minority carriers whereas holes are the majority carriers.

A N-type semiconductor is an intrinsic semiconductor (e.g. silicon Si) in which a donor impurity (e.g. arsenic As in Si, or Si in GaAs) has been intentionally introduced. The impurities are called donor impurities since they have to give an extra electron to the conduction band in order to make all the bonds with neighboring atoms (As is pentavalent while Si is tetravalent). N-type semiconductors has a higher electron density n and a lower hole density p than the same intrinsic semiconductor. Holes are said to be the minority carriers whereas electrons are the majority carriers.

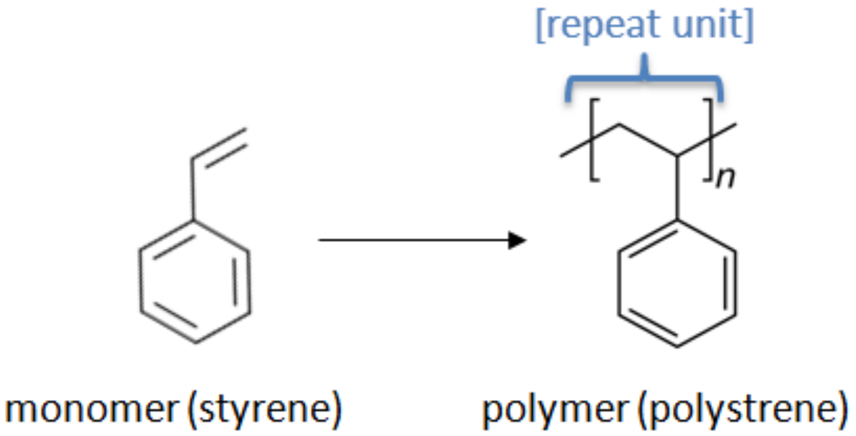
Polymers

Another staple material that have diverse application are Polymers. Plastics may first come in mind when we talk about Polymers, but surprisingly, they are more available than that. Plastics is just one of the Synthetic types, with the most familiar ones such as PET in bottles, PVC in pipes, and Polystyrene in Styrofoam cups. The Natural have an even more diversified pool of functional materials. For example, Cellulose in plant fibers, Chitin on mollusks, Keratin in your hair, Proteins in muscular fibers, and the all-important Nucleic acids is polymerized as our DNA. Actually, we owe so much of life’s robust persistence from the strength borrowed from these Natural Polymeric materials. Nature had solved its own life engineering problems using these Polymerized substances. Today we had researched extensively this knowledge, and it had helped us develop our own synthetic Polymeric materials with as much diversified applications as we have seen nature rely on them.

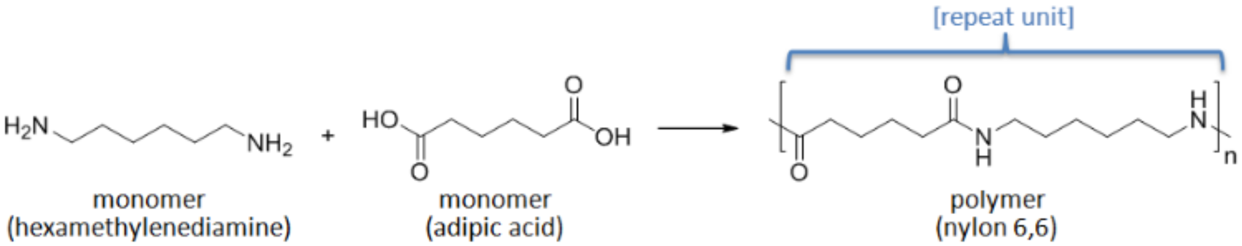
Understanding the molecular picture of these Polymeric materials would be one of the most interesting and useful knowledge we could get from studying Material Science, because what we would be studying is almost akin to life itself.

A. Classification of Polymers

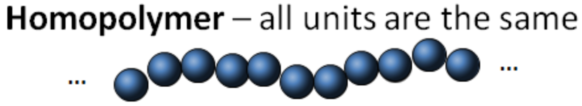
The word “polymer” can be broken down into the Greek components: poly (many) + mer (part). “One part” would then be called a monomer, “two parts” would be a dimer, “three parts” a trimer, “a few parts” is an oligomer. Polymers can be made of a single repeating unit, over and over. There could also be many different monomers in a polymer, they can have ordered repeats, they can have random repeats, and could extend to an infinite combination of different monomers whose structures would be further categorized and talk about later in detail. Thus, a polymer what we call a Macromolecule, or a molecule that is quite large because of their capacity to chain these multiple covalent bonds.



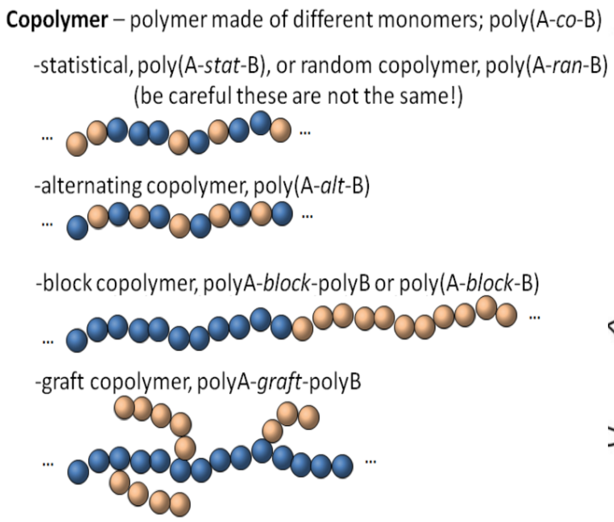
Take Polystyrene on the above figure for example. Styrene is the name of the monomer, and Polystyrene is made up of this monomer “repeat units” making up the polymer molecule. Note that the repeat unit is chemically different from the monomer because it had already reacted, as we see the double bond disappears on the polystyrene chain. A repeat unit can be made from multiple monomers. A good example of this would be nylon 6,6 produced from the polymerization of hexamethylenediamine and adipic acid (Analyze the figure below). Notice that the repeat unit of nylon 6,6 is a combination of both monomers, and that some atoms were lost during the polymerization so that the chemical structure of the repeat unit is not just the simple addition of both monomers; we have lost H_2O in this reaction.

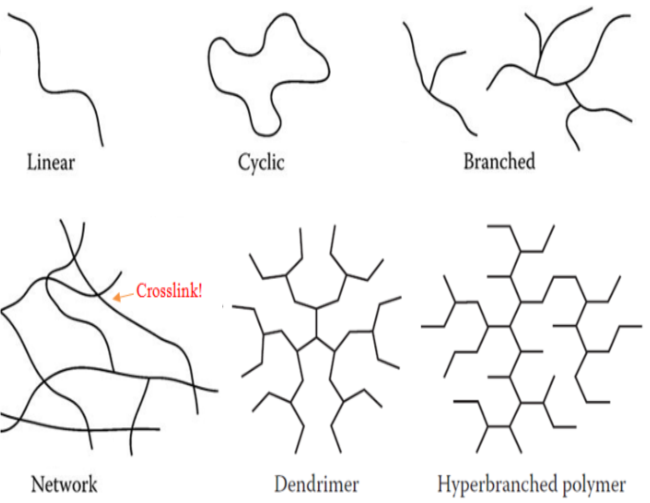


If the number of atoms, which is commonly expressed as molecular weight, of the monomer is the same as the repeat unit, then this process is called a polyaddition polymerization. However, the number of atoms in the repeat unit is not always the same as the monomer. If there are chemical byproducts of the polymerization, then this polymer is a result of the process we call a polycondensation polymerization.



Depending on how many different monomers are combined into a polymer, and in what order and structure, we have different ways of generally classifying polymers. If the polymer is made up of a single monomer, we call it a homopolymer. If a polymer is derived from the polymerization of multiple different monomers, we call it a copolymer. There are many varieties of copolymers. Refer to the figure below and note the differences of each.





These monomer strings could be imagined as tiny pieces of yarns – and in a simplified way could be drawn as a "skeletal structure" just as shown in the upper right figure. In such diagrams, the specific chemical structure is not drawn but the lines are supposed to represent the polymer backbone that helps visualize the higher order structure of these strings. Because a polymer doesn't just have to be a linear – it can be much more complicated than that. It can be branched – like a tree – or it can be network, where all the strings are connected to each other at linking points called crosslinks. The skeletal structure of a polymer significantly affects its properties. For example, network polymers tend to hold their 3D shape much better than linear polymers.

In addition to classifying polymers by their structure, we also classify them based on their physical properties. There are three main types: thermoplastics, elastomers, and thermosets. Elastomers are stretchy – think "elastic", like a rubber band. Because most elastomers are network polymers, they can be stretched and deformed and return to their original shape due to their 3D structure being held together by crosslinks. Their unique properties are a function of their 3D network structure. Things like crosslink density affect their macroscale material properties. Thermosets are rigid that usually have a very high degree of crosslinking. When they are heated, they don't often flow or soften, they usually just degrade with bonds within the polymers getting broken. This is in contrast to thermoplastics or thermosoftening polymers which do flow upon heating. Thermoplastics are typically linear or branched and do not have that network structure to hold their shape, hence they flow when heated. Most commercial polymers are thermoplastics. They can be crystalline, semi-crystalline, or amorphous. Crystalline phases have a melting temperature (T_m). Amorphous phases can't really "melt" because they are already amorphous (it's not considered a phase transition), so we use the term glass transition temperature (T_g) to characterize this softening point.

B. Assessing Polymer Size

How big is a polymer? Usually "short" polymers are called oligomers. When we start getting to tens, hundreds, thousands of repeat units or more, then we have polymers. In general chemistry we learned how to calculate the molar mass of a molecule. Similarly, we can describe the "size" of a polymer using molar mass (or molecular weight) which is typically defined in units of g/mol and abbreviated as "M". Another way of describing the size of a polymer is by its degree of polymerization. Degree of polymerization (described by "x") is the number of repeat units in a polymer. If we know the molar mass of a polymer, we could figure out the degree of polymerization and vice versa given that we know the molar mass of the repeating unit.

This relationship is set up on the following equation, where the new variable M_o is the molar mass of the repeat unit:

$$M = x*Mo$$

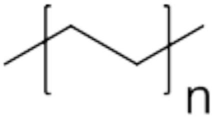
Where:

- M = molar mass
- x = degree of polymerization
- Mo = molar mass of the repeat unit

We see that the total molar mass of the polymer is just a function of the degree of polymerization and the molar mass of the repeat unit. Newer students that are unfamiliar to skeletal diagrams of molecule should refer to basic organic chemistry on how to count C,H,O atoms in such diagrams.

I.) PROBLEM TYPE#1: Molar Mass of Polyaddition Polymers

What is the molar mass of polyethylene (shown below) which has a degree of polymerization of 100?

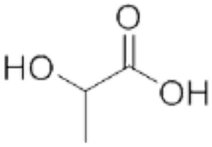


1.) Determine the molecular formula of the repeat unit:
Mo = 2*C + 4*H (*Refer to Organic Chemistry*)
Mo = 2*12 +4*1 = 28 g/mol

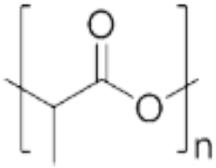
2.) Calculate polymer molar mass, M = x*Mo:
M = x*Mo = 100*(28g/mol) = 2,800 g/mol

II.) PROBLEM TYPE#2: Molar Mass of Polycondensation Polymers

The following monomer is polymerized (condensation polymerization with loss of water). If the degree of polymerization is 100, what is the molar mass of the polymer?



1.) First, draw the polymer in terms of the repeat unit:



2.) Determine the molecular formula of the repeat unit:
3 Carbon, 2 Oxygen, 4 Hydrogen

3.) Calculate the molar mass of the repeat unit, Mo:
3 (12 g/mol) + 2 (16 g/mol) + 4 (1 g/mol) = 72 g/mol

4.) Calculate polymer molar mass, M = x*Mo:
M=100∗72gmol=7,200 g/mol

For statistical copolymers with more than one monomer, or more than one type of repeat unit, we define the mean (Mo') of the copolymer as just a weighted average of the repeat unit, where the weights are the mole fraction (Xj) of each type of repeat unit (Mj0). The previous equation would still be applied using the weighted average this time.

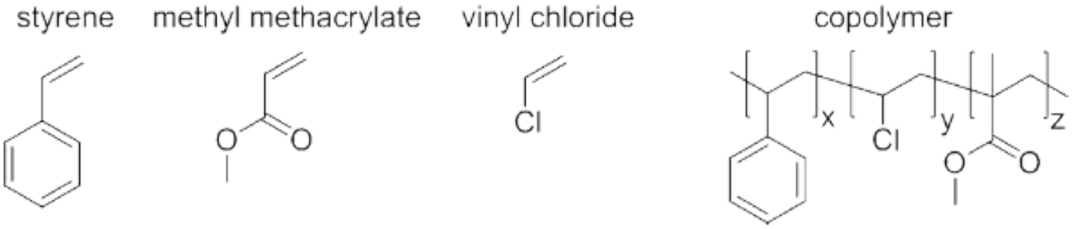
$$Mo' = \sum XjMj0$$
$$M = x*Mo'$$

Where:

- Xj = mole fraction of each type of repeat unit (j)
- Mj0 = molar mass of each type of repeat unit (j)
- Mo' = weighted average of the repeat unit

III.) PROBLEM TYPE#3: Molar Mass of Statistical Copolymers

What is the mean molar mass of the repeat unit for a copolymer comprised of 20 mol% styrene, 30 mol% methyl methacrylate, and 50% vinyl chloride? The chemical structures of the monomers and the resulting copolymer are shown below. What is the Molecular Mass if the degree of polymerization is 35?



1.) Compute for the weighted average of the repeat unit, Mo'.:
Mo' =0.2*104g/mol+0.3*100g/mol+0.5*62.5g/mol= 82.05g/mol

2.) Calculate polymer molar mass, M = x*Mo:
M = x*Mo' = 35*82.05g/mol = 2871.75 g/mol

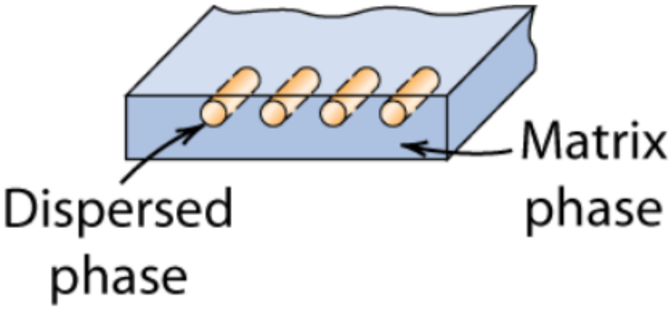
Composites and Nanomaterials

The structure of materials can be classified by the general magnitude of various features being considered. The three most common major classification of structural, listed generally in increasing size, are:

Atomic structure, which includes features that cannot be seen, such as the types of bonding between the atoms, and the way the atoms are arranged. Microstructure, which includes features that can be seen using a microscope, but seldom with the naked eye. Macrostructure, which includes features that can be seen with the naked eye) The atomic structure primarily affects the chemical, physical, thermal, electrical, magnetic, and optical properties. The microstructure and macrostructure can also affect these properties but they generally have a larger effect on mechanical properties and on the rate of chemical reaction. The properties of a material offer clues as to the structure of the material.

A. Composite Materials

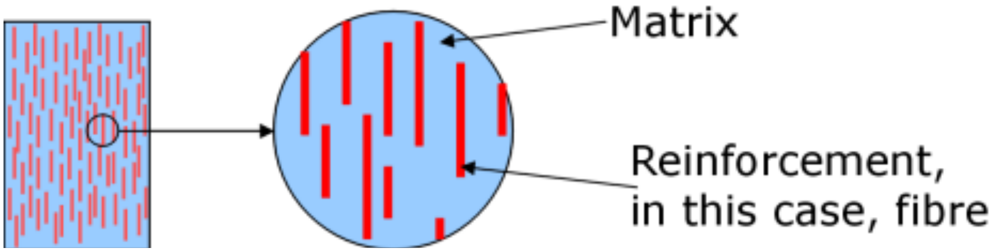
Composite materials are materials which are a combination of two or more distinct individual materials. These combinations are formed to obtain a more desirable combination of properties. This is called the "principle of combined action". One example of this principle is the use of composites for aircraft structures. These composites are designed to be lighter weight with comparable strength to metal structural elements that they are replacing. Most composites in use today have been created to have improved stiffness, toughness, and ambient and high-temperature strength. Typically, a composite is formed with a continuous phase called the matrix. As shown in the figure below, the matrix phase surrounds another phase which is discontinuous and referred to as the dispersed phase.



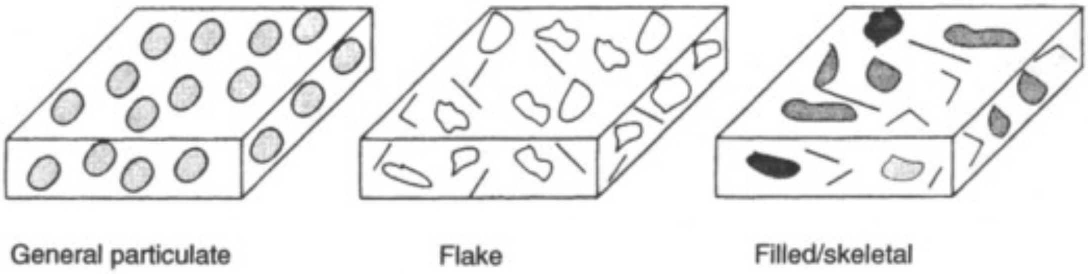
The purpose of the matrix phase is to keep the dispersive phase in place, transfer stress to the dispersed phase, and protect the dispersed phase from the environment. The purpose of the dispersed phase typically depends on which material type it is composed of:

- Metal dispersive phases – used to increase yield strength, tensile strength, and/or provide stability over the life of the product.
- Ceramic dispersive phases – used to produce materials which resist fracture.
- Polymer dispersive phases – used to increase the modulus of elasticity, yield strength, tensile strength, and/or provide stability over the life of the product.

Furthermore, Composites are typically classified by the type of dispersive phase used: fiber reinforced, particle reinforced or structural.

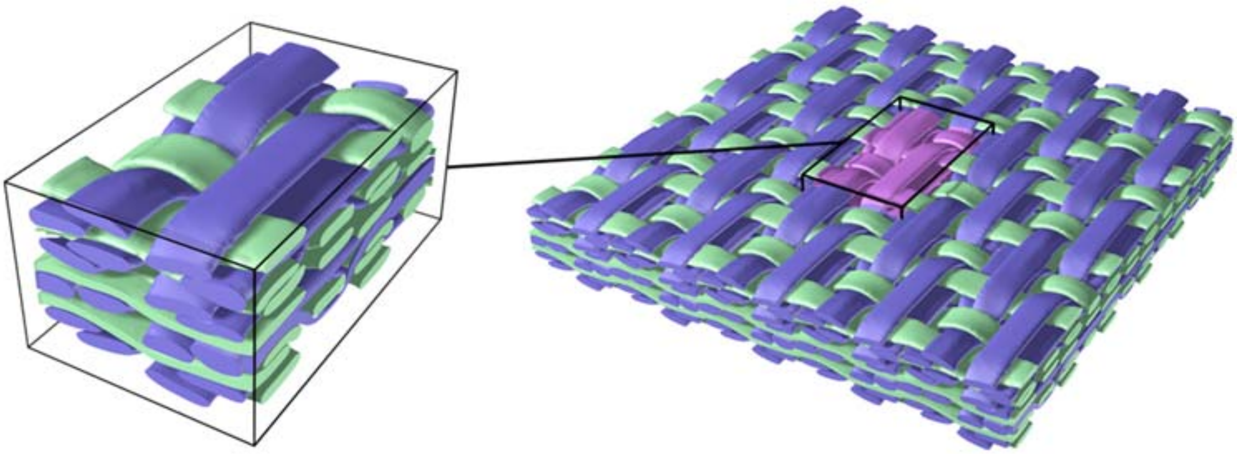


Fibre reinforced composites are classed as either continuous (long fibres) or discontinuous (short fibres). When the fibres are aligned they provide maximum strength but only along the direction of alignment. The composite is considerably weaker along other directions and is therefore highly anisotropic. Components that require strength in one particular direction will use aligned fibres while components that require strength in more than one direction will use randomly oriented fibres. Composites that have fibres aligned in one principal direction are made using either continuous or discontinuous fibres. Composites with randomly oriented fibres are usually made with discontinuous fibres. Composites are essentially tailor made materials in that there are a number of parameters, other than the properties of the fibres and matrix, that can be changed to meet the design requirements of a given application.

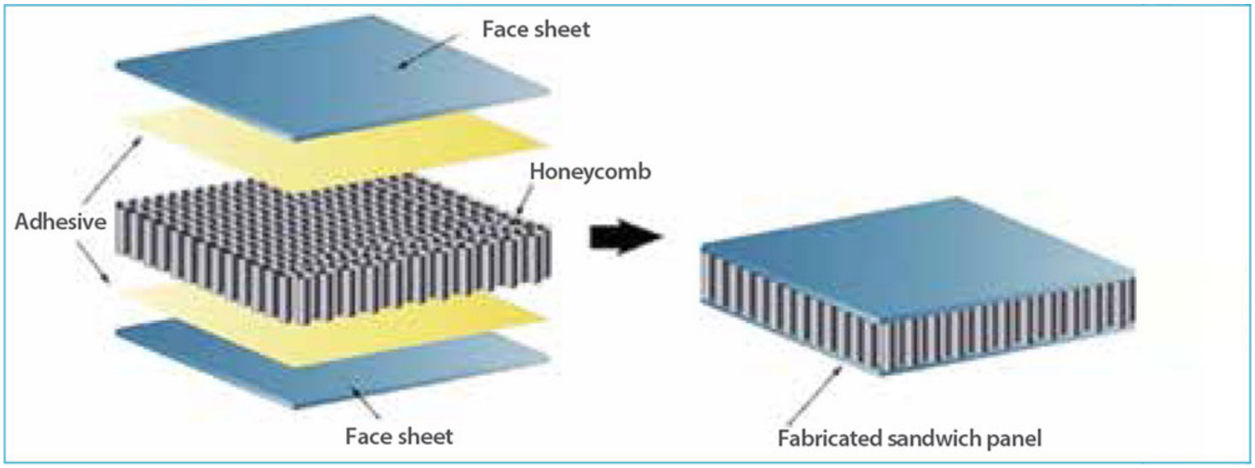


Particle reinforcing in composites is a less effective means of strengthening than fibre reinforcement. Particulate reinforced composites achieve gains in stiffness primarily, but also can achieve increases in strength and toughness. In all cases the improvements are less than would be achieved in a fibre reinforced composite. Particulate reinforced composites find applications where high levels of wear resistance are required such as road surfaces. The hardness of cement is increased significantly by adding gravel as a reinforcing filler. The principal advantage of particle reinforced composites is their low cost and ease of production and forming.

Structural composites are multi-layered and designed to have low densities and high degrees of structural integrity. Different layers of materials are stacked by different structural design, and the kind stacking acts as additional reinforcement. Two of the most common structural composites are 3D woven composites and Sandwich composites.



Three-dimensional composites use fiber preforms constructed from yarns or tows arranged into complex three-dimensional structures. These can be created from a 3D weaving process, a 3D braiding process, or a 3D lay of short fibers. A resin is applied to the 3D preform to create the composite material. Three-dimensional composites are used in highly engineered and highly technical applications in order to achieve complex mechanical properties. Three-dimensional composites are engineered to react to stresses and strains in ways that are not possible with traditional composite materials composed of single direction tows, or woven composites, or stacked laminate materials.

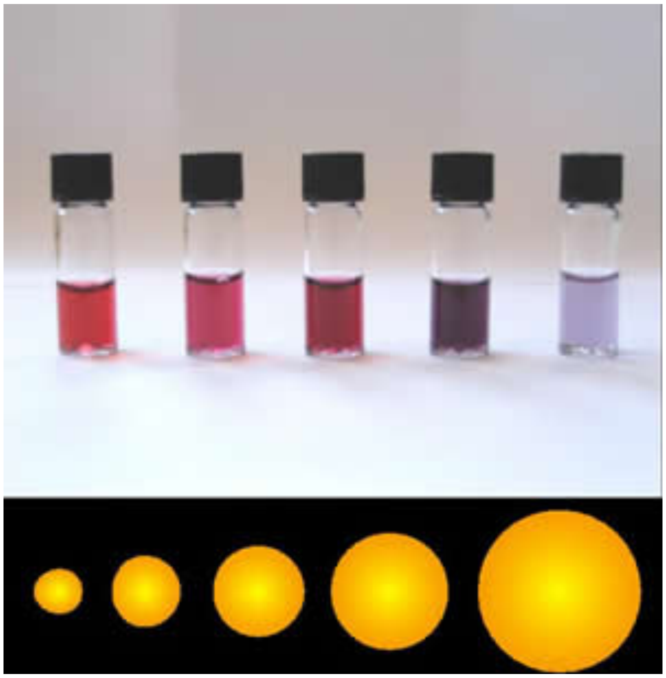


A sandwich-structured composite is a special class of composite materials that is fabricated by attaching two thin but stiff skins to a lightweight but thick core. The core material is normally low strength material, but its higher thickness provides the sandwich composite with high bending stiffness with overall low density. Open-and closed-cell structured foams like polyethersulfone polyvinylchloride, polyurethane, polyethylene or polystyrene foams, balsa wood, syntactic foams, and honeycombs are commonly used core materials. Sometimes, the honeycomb structure is filled with other foams for added strength. Open- and closed-cell metal foam can also be used as core materials. Laminates of glass or carbon fiber-reinforced thermoplastics or mainly thermoset polymers (unsaturated polyesters, epoxies...) are widely used as skin materials. Sheet metal is also used as skin material in some cases. The core is bonded to the skins with an adhesive or with metal components by brazing together.

Lastly, structural engineering could also be applied into the nanoscale. These materials are known as Nanocomposites, have the dimensions of the dispersed phase particles are on the order of nanometers. This size range allows for some unusual properties that could not be accessed on a larger particle size otherwise. We will discuss these nano effects on the following section.

B. Nanomaterials

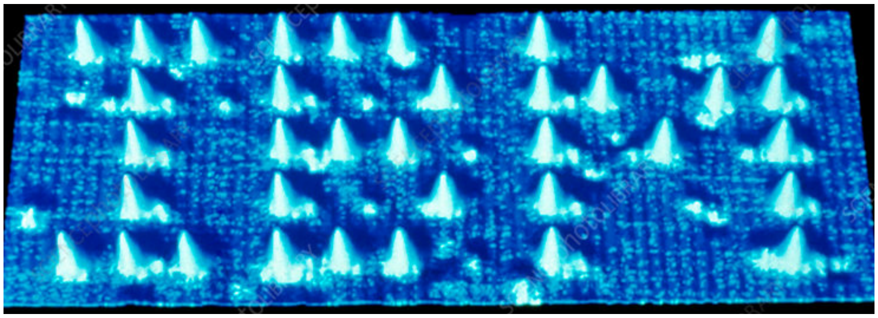
Nanotechnology involves the control of atoms and molecules to produce materials in the size range of 1 – 100 nm, whose size or geometry dominate their material properties. Nanotechnology occurs in a size range were quantum mechanics dominate, but the materials are larger than a single atom. This size range is the range where single atom behavior is transitioning to bulk material behavior. This allows for the tuning of properties to desirable results, which allows for the creation of designer materials. An example of this is gold nanoparticles. As shown in the figure below, nano-sized gold particles range in color from bright red, pink, purple, to blue, depending on the size of the nanoparticles.



So, how many atoms are we talking about when we say the material ranges from 1 to 100 nm in size? A cube of 1 nm on a side would have around 100 atoms, while a cube of 100 nm on a side would have around 100 million atoms. That is quite a range. Calculating the number of atoms that would be on the surfaces of 1 nm nano cubes and 1 cm bulk cube shows that in the nano cube, 60% of the atoms were on the surface of the cube. This was in stark contrast to the bulk cube, where only one out of 109 atoms were on the surface.

What does this mean chemically? Bulk gold is highly unreactive; it does not tarnish, it does not react with other metals, etc. It is so unreactive that it's possible to find gold in nature in its native state, gold nuggets. Nanogold, on the other hand, is extremely reactive. In bulk gold, the atoms are overwhelmingly non-surface atoms. These non-surface atoms have sufficient neighboring atoms to satisfy their bonds. In nanogold, most of the atoms are on the surface and possess unsatisfied bonds, which makes them extremely chemically reactive. This is a case where the size of the particle matters but also the geometry matters. In the case of nano gold, the geometry of possessing mostly surface atoms results in a chemically active material.

Nanotechnology, through the control of atoms and molecules, has the potential to create unique materials with wide-ranging applicability including the areas of medicine, smaller (faster) devices, self-assembled structures, and other designer materials applications. Nano materials are also allowing scientists to explore still unanswered fundamental materials questions. The field of nanotechnology is generally accepted to have been identified by Nobel laureate Richard Feynman during a futuristic talk entitled, "There’s Plenty of Room at the Bottom," in 1959. In that presentation, Feynman speculated about being able to write the entirety of the Encyclopedia Britannica on the head of the pin. On September 28, 1989, an IBM physicist, Don Eigler, became the first person to manipulate and position individual atoms. One example of his work is shown in the figure below utilizing 35 xenon atoms.



As our understanding, and control, of materials at the nanometer scale improves, we are able to manufacture materials that are: tailored for specific tasks, designed to perform at the extremes of materials properties, or can utilize structure to enable properties not achievable before. Utilizing bottom-up, self-assembly, and other novel fabrication techniques, designer materials are becoming possible for everyday usage. In fact, superior materials are known today, but their utilization is hampered by our current inability to mass produce usable quantities economically. In this lesson, we looked at the basics of electronics, as well as some of the basics of nanoelectronics, which has the potential of being the electronics of the very near future.

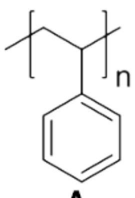
Activities/Assessments:

1. Explain what are electron clouds and how do they differ from our traditional picture of an electron. Are they waves or are they particles? Research on the reasons why so.

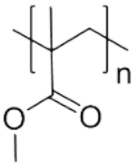
2. What are quantum numbers and how do they relate to energy levels? How does the Band Theory of Metal utilize and incorporate these energy levels through the Valence Band and Conduction Bands?

3. A statistical copolymer formed from addition polymerization of acrylamide (71 g/mol) and methyl methacrylate (100 g/mol) has a molar mass of 11,955 g/mol with degree of polymerization of 150. What is the molar fraction of acrylamide?

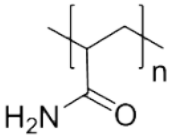
4. A polymer with molar mass of 35,200 g/mol. has a degree of polymerization of 800. Which polymer, of the ones shown below, could it be? Show your solution. (Refer to basic organic chemistry on how to count C,H,O atoms in skeletal structures such as shown below)



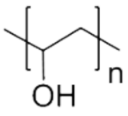
A



B



C



D

5. Research on the structures of Natural Polymers such as Keratin, Cellulose and Chitin. Give examples on where these polymers occur in nature, their main functions and examples of organisms utilizing them.

6. Carbon Fiber and Fiber Glass are two of the most used composite materials. Diagram and explain what they are made of and what materials are they composed.
7. Why are particles measuring at 300nm ~ 1000nm not classified as a Nanomaterial? Should they be considered as Nanomaterials or not? Explain the reason for the rigid classification and the properties exclusive to the “Nanomaterial” region.

LESSON 10: CHEMISTRY OF THE ATMOSPHERE
UNIT 1: The Composition of the Atmosphere

Introduction:

Human beings can survive for couple days in the absence of water but this is not the same in the case of air. The air that we breathe is part of the atmosphere. In this lesson, the layers and composition of the atmosphere is revisited.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1) Describe how the different layers of the atmosphere are characterized.
2) Discuss how the change in the lapse rate at the troposphere affect the life on earth.
3) Enumerate the components of the atmosphere.

Course Materials:

Air and the Atmosphere

Air is the term used to describe the homogeneous mixture of gases that makes life on earth sustainable due to its dioxygen molecule component while the ***atmosphere*** refers to the thin air that is made up of a low-density fluid that extends few hundred kilometers from the surface of the earth thus surrounding the planet.

The layers of the atmosphere

The atmosphere is subdivided into different layers in accordance to their temperature profile (Figure 1).

The **troposphere** is the lowest part of the atmosphere. It is where the planet Earth's weather and air pollution takes place. It extends from the ground level to 1- to 15 km. The temperature change within the troposphere with respect to altitude (known as lapse rate) decreases at a rate of 5 to 6 K/km. The troposphere is the occurrence of earth's weather and air pollution.

An unwanted phenomenon may occur in the troposphere, known as thermal inversion. This happens when the lapse rate becomes positive; hence, the reversal of the normal behavior in the troposphere wherein the cold air at the surface of the earth is overlaid by the warmer air. Thermal inversion changes the dynamics of air movement resulting in air pollutants to be trapped near the earth's surface. Prolong occurrence can have several adverse effects on the population's health such as lung inflammation.

The tropopause is the layer of atmosphere of constant temperature found between the troposphere and the stratosphere.

Above the tropopause, is the **stratosphere**. It has a temperature profile that increases with the altitude up to a maximum of about 273K and it reaches at around 50 km from the surface of the earth. The layer's temperature profile is what suppresses air to undergo vertical motions.

The stratopause is the layer of atmosphere of constant temperature found between the stratosphere and the mesosphere.

Above the stratopause is the **mesosphere** with a temperature profile that is similar to the troposphere, that is the temperature increases as the altitude increases until it reaches the mesopause at an altitude of 85 km from the surface of the earth. In this layer, the gases are thick enough to slow down the meteors hurtling to the atmosphere, which when burn up leave fiery tails in the night sky.

The mesopause is the layer of atmosphere of constant temperature found between the mesosphere and the thermosphere.

Above the mesopause is the **thermosphere** with a lapse rate of 5K/km.

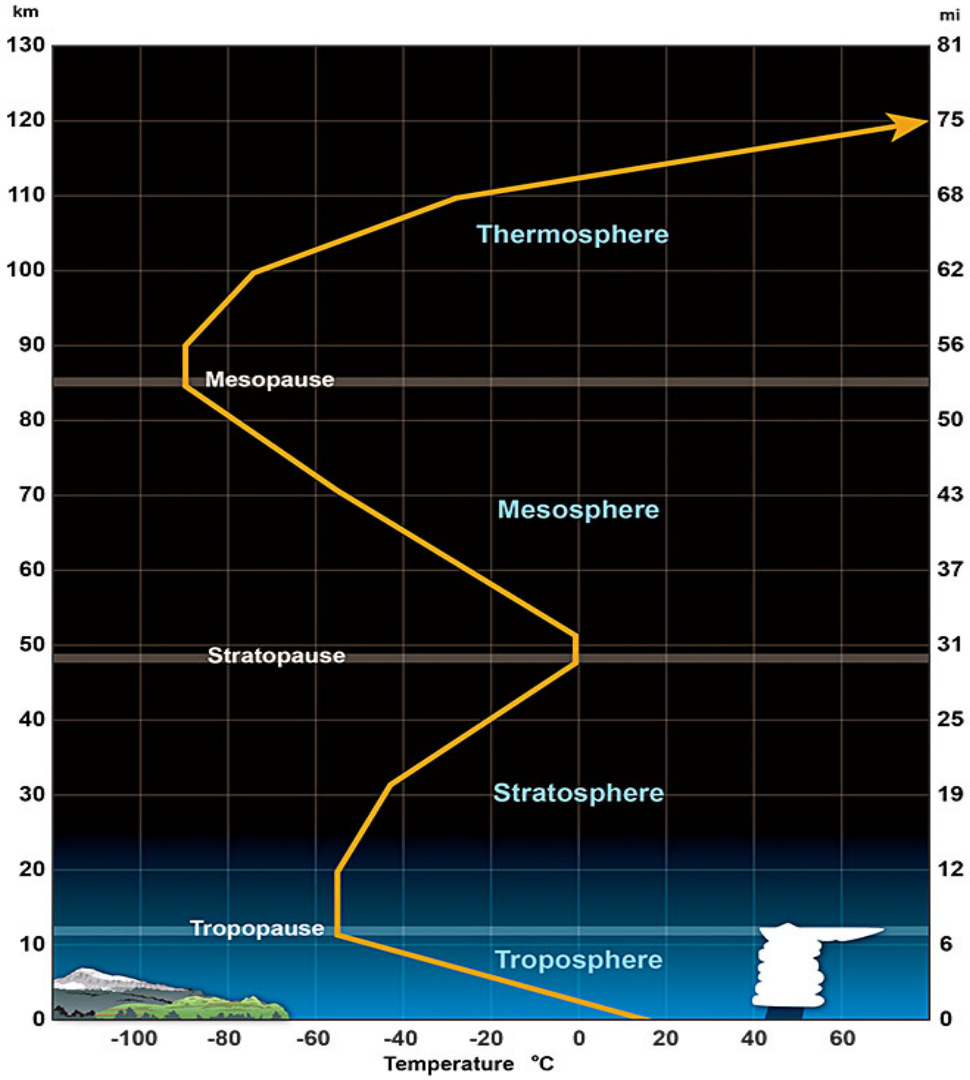


Figure 1: The Temperature Profile of the Atmosphere. Image source: www.weather.gov/jetstream/layers

The thermopause is the layer of atmosphere of constant temperature found between the thermosphere and the exosphere.

The outermost layer of the atmosphere is the **exosphere** which extends from the thermopause to about 10000 km from the surface of the earth. It is in this layer where satellites orbit the earth.

The components of the atmosphere

The atmosphere is a homogeneous mixture of various gases. Its main composition has remarkably steady for ages with nitrogen and oxygen being the main components. It is the abundance number of oxygen molecules in the atmosphere that makes life possible on earth.

COMPOSITION OF THE ATMOSPHERE

Gas	Percentage
Nitrogen	78%
Oxygen	21%
Argon	0.90000%
Carbon dioxide	0.03000%
Neon	0.00200%
Helium	0.00050%
Methane	0.00020%
Krypton	0.00010%
Hydrogen	0.00005%
Dinitrogen oxide	0.00005%

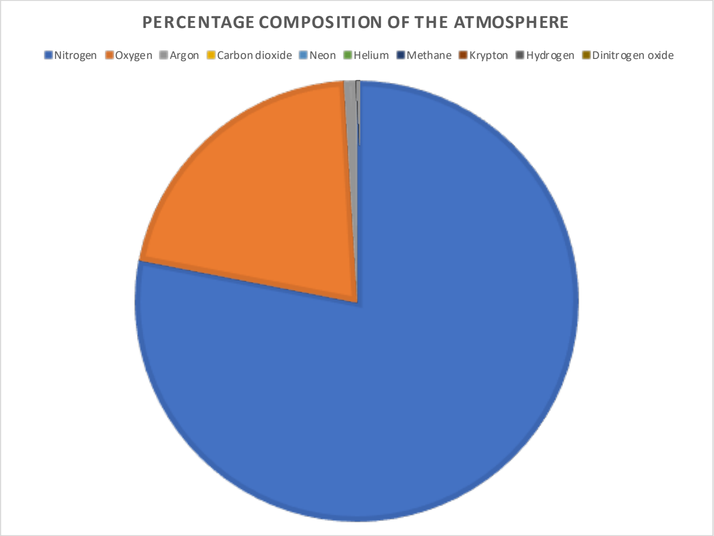


Figure 2: Composition of the Atmosphere

Activities and Assessment:

1. What are the different layers of the atmosphere and how they were characterized from each other?
2. What is thermal inversion and how does it occur? Describe how its occurrence produce adverse effect to humanity.
3. Name the main components of the earth's atmosphere?

LESSON 10: CHEMISTRY OF THE ATMOSPHERE
UNIT 2: Processes in the Atmosphere

Introduction:

Each of the layers of the atmosphere has distinct characteristics and compositions that influence the processes occurring therein. In this lesson, chemical process that are occurring in the troposphere and stratosphere are discussed.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1) Describe the impact of the processes in the troposphere on air quality.
2) Discuss how the stratospheric ozone works.
3) Describe how aerosols affect the earth's temperature and climate.

Course Materials:

Processes occurring at the troposphere

The composition of the stratosphere is dependent on the properties of gases that are present at the troposphere and the processes they undergo. If the trace gases in the troposphere are inert and do not react with the available free radicals, they will be transported to the stratosphere. Examples of these gases are chlorofluorocarbons (CFCs) and methyl chloride. However, there are trace gases that readily react to free radicals and sometimes cause formation of unwanted compounds in the atmosphere.

The presence of these free radicals in the troposphere are crucial to the formation of compounds that are responsible to pollution. According to the work Hiram I.I. Levy entitled "Photochemistry of minor constituents in the troposphere", the reaction of the $^{\bullet}OH$ radical with methane and nitrogen dioxide produces carbon monoxide and nitric acid, respectively.

While dioxygen molecules are abundant in the atmosphere, they are not considered as the principal oxidative species in the troposphere. This is because reactions of dioxygen molecules require higher activation energy compared to that of the free radicals such as the hydroxyl radical, $^{\bullet}OH$. Where are there free radicals come from?

Major sources of $^{\bullet}OH$ is the ozone photolysis with ultraviolet (UV) radiation during daytime, producing excited oxygen atom which rapidly reacts with water vapor.

$$O_3 + hv \rightarrow O_2 + O$$

$$O + H_2O \rightarrow 2 \cdot OH$$

During night time, the nitrite radical $^{\bullet}NO_2$ reacts with ozone (O_3) to produce the nitrate radical $^{\bullet}NO_3$.

$$NO_2 \cdot + O_3 \rightarrow NO_3 \cdot + O_2$$

Moreover, when the compound peroxyacetyl nitrate (PAN, $CH_3COOONO_2$) thermally decomposes in the presence of $NO^\bullet$ also produce $^\bullet OH$ radicals and convert $NO_2^\bullet$

$$CH_3COONO_2 \rightarrow CH_3CO_3 + NO_2\cdot$$

$$CH_3CO_3 + NO\cdot \rightarrow CH_3CO_2 + NO_2\cdot$$

$$CH_3CO_2 + O_2 \rightarrow CH_3O_2 + CO_2$$

$$CH_3O_2 + NO\cdot \rightarrow CH_3O + NO_2\cdot$$

$$CH_3O + O_2 \rightarrow CH_2O + HOO\cdot$$

$$HOO\cdot + NO\cdot \rightarrow \cdot OH + NO_2\cdot$$

$$CH_2O + \cdot OH \rightarrow CHO + H_2O$$

$$CHO + O_2 \rightarrow CO + HOO\cdot$$

$$HOO\cdot + NO\cdot \rightarrow \cdot OH + NO_2$$

Processes occurring at the stratosphere

The stratosphere is where the ozone layer can be found. Stratospheric ozone protects life in the surface of the earth by screening the harmful ultraviolet rays from the sun through the photodissociation mechanism.

$$O_3 + hv \rightarrow O_2 + O\cdot$$

$$O\cdot + O_2 \rightarrow O_3$$

The ozone in not consumed and the UV radiation is converted into heat. This is the reason behind the positive lapse rate profile of the stratosphere. Because the stratosphere is warmer compared to the troposphere, an inversion between the two layers occur. This traps the molecules found in the troposphere.

On the other hand, O_2 can be consumed if $O^\bullet$ collides with O_3, the process known as the recombination reactions. This process is very slow and if it is the only means by which O_3 is consumed, then the ozone layer will be thicker than it really is.

$$O_3 + O\cdot \rightarrow 2O_2$$

Another way by which O_3 is consumed is catalysis of the recombination reactions by available free radicals such as $NO^\bullet$, $NO_2^\bullet$, $H^\bullet$, $^\bullet OH$, $HO_2^\bullet$, $Cl^\bullet$, $ClO^\bullet$ and $ClO_2^\bullet$.

The thickness of the ozone layer is therefore due to the competition among these three reactions.

Aerosols

It is not only the gaseous compounds that have impact to the atmospheric conditions. Solid and liquid particulates, known as aerosols, also have consequences in atmospheric temperature and climate because they have the ability to alter the radiative processes of the Earth. An example of which is the soot as a product from the burning of fossil fuels.

Activities and Assessment:

1. The free radicals that are found in the troposphere have a significant role in air pollution. Discuss the mechanisms by which they were produced.
2. Elaborate the meaning of the statement: “The thickness of the ozone layer is therefore due to the competition among these three reactions”.
3. How do aerosols affect the earth’s atmospheric conditions?

LESSON 10: CHEMISTRY OF THE ATMOSPHERE
UNIT 3: Air Pollution, Sources and Effects

Introduction:

The atmosphere has its own ways of recreating the balance to make life sustainable for all its habitats. However, changes occur due the presence of pollutants in the atmosphere. In this lesson, we are to discuss the common compounds that pollute the air and how they do it.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1) Enumerate the ten groups of air pollutants and discuss their respective sources and effects.
2) Discuss how the incomplete internal engine combustion adds to air pollution.
3) Describe how greenhouse gases enhance the greenhouse effect.
4) Discuss the chemical reactions behind photochemical smog formation, stratospheric ozone destruction and acid rain formation.

Course Materials:

Air Pollutants

Air pollutants are products and by-products of different process such as combustion, industrial activities, natural resource processing and commercial services. They can be classified as ***primary pollutants*** (those that are directly emitted to the atmosphere) and ***secondary pollutants*** (those that are products of various chemical reactions in the atmosphere). There are ten groups of air pollutants according to the US EPA (Environment Protection Agency) official Hazardous Air Pollutants (HAPs) list:

1. Carbon dioxide (CO_2) and Carbon monoxide (CO)

   Carbon dioxide is produced from complete combustion of fuels and metabolic processes while carbon monoxide is derived from the incomplete combustions processes and from the photochemical transformation of volatile organic compounds (VOCs) by the free hydroxyl radical ($^{\bullet}OH$) generated in the atmosphere such as methane.

$$CH_4 + \cdot OH \rightarrow CH_3 \cdot + H_2O$$

$$CH_3 \cdot + O_2 + hv \rightarrow CO + H_2 + \cdot OH$$

   Carbon dioxide is considered toxic because it can replace oxygen uptake by hemoglobin.

2. NO_x: Nitrogen oxide (NO), nitrogen dioxide(NO_2) and dinitrogen oxide (N_2O)

   Nitrogen oxide is a product of combustion through the oxidation of air nitrogen at high temperature and can also be produced by lightning. It can also oxidize into nitrogen dioxide which is a precursor of acid rain and smog formation. Meanwhile, the dinitrogen oxide is released by soil bacteria and can be converted as nitrogen oxide into the atmosphere.

3. SO_x: Sulfur dioxide (SO_2) and sulfur trioxide (SO_3)

   Sox are produced from the oxidation of sulfur-containing fuels and dihydrogen sulfide, H_2S. H_2S is a toxic gas that is produced from biological decay of organic matter and various human activities such as geothermal and industrial processes.

$$H_2S + O_3 \rightarrow H_2O + SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

4. Photochemical oxidants

   Photochemical oxidants are considered as secondary pollutants as they are products of chemical reactions from other pollutants. The common photochemical oxidants are ozone (which can be produced through lightning or photochemical reactions), peroxybenzonyl nitrate (PBzN), peroxyacyl nitrate (PAN), hydroxyl radicals ($^\bullet OH$) and nitrogen oxide derivatives. In was seen from the previous lesson on how free radicals react with other compounds in the atmosphere.

5. Particulates and aerosols

   Particulates and aerosols are complex mixture of extremely small particles and liquid droplets. They are existing in different forms such as ocean salt crystals, soil particles, minerals and metallic compounds. These small particles may come from wild fires, volcanic eruptions, incomplete combustion, mineral processing, industrial processing among others. The two most common particulates are the PM2.5 and PM10. PM2.5 are those that has an average diameter od $\leq 2.5\mu$ and is considered dangerous because they are often carcinogenic yet the body is not able to release them. Moreover, they are also active in smog formation and other photocatalytic activities. PM10, on the other hand, are those that have diameters within the range of $2.5\mu m \leq d \leq 10\mu m$.

6. Metal and metalloid compounds and vapors

   These may consist of hazardous particulate matter or vapors of metals such as Pb, Hg, As, Ni, Be, and Cu that are generated by combustion and incineration processes, engine wear, lubricating oil components, lamp wastes, and mineralization of geologic formations.

7. Polycyclic aromatic hydrocarbons and derivatives (PAHs)

   These are aromatic compounds of at least three fused aromatic rings and are hazardous. They are products of incomplete combustion of fossil fuels and vegetable matters, petroleum products and petroleum refineries.

8. Volatile organic compounds (VOCs)

   These are light hydrocarbons and unsaturated hydrocarbons and are precursors to smog formation and organic aerosols. They usually come from incomplete combustion processes, fugitive sources, industrial processes, petroleum processing and solvent intensive processes such as painting.

9. Halogenated hydrocarbons and polychlorinated organic compounds

   Hazardous compounds volatile chlorinated hydrocarbons and polychlorinated dibenzo compounds dioxins and furans belong to this category. They usually come from incineration processes and car emission. The ozone layer destructing chlorofluorocarbons (CFCs) are also included in this category.

10. *Radionuclides*

    Their presence is due to natural gas or particulate emissions from natural deposits of uranium where radon is liberated, as well as emissions from uranium processing, nuclear reactors, and fuel-reprocessing wastes.

Internal Engine Combustion Process

Combustion of fossil fuel leads to the production of main primary pollutant CO, NOx, VOCs and SO_2.

The combustion equation of an internal engine that is ideally operating is given by the equation below:

$$C_nH_m + \left(n + \frac{m}{4}\right) O_2 \rightarrow nCO_2 + \left(\frac{m}{2}\right) H_2O$$

If the hydrocarbon (C_nH_m) to oxygen ratio is not adequate, unreacted hydrocarbons and partially oxidized carbon will be emitted to the atmosphere. Moreover, with an excess O_2, NO production is favored as it reacts with a sufficient amount of nitrogen in the atmosphere:

$$N_2 + O_2 \leftrightarrow 2\,NO$$

$$2NO + O_2 \leftrightarrow 2NO_2$$

In addition, the sulfur content of the fuels generated sulfur dioxide upon burning:

$$S + O_2 \rightarrow SO_2$$

The Greenhouse Effect

The greenhouse effect (Figure 1) is a natural process by which earth maintains the heat on its surface to make life sustainable. Solar radiation passes through the clear atmosphere wherein most of the radiation are absorbed by the earth's surface which keeps its warmth. Some of the heat from the earth radiates towards space but some of it is trapped by the greenhouse gases in the atmosphere. This keeps the planet warm enough to sustain life. However, the concentration of greenhouse gases in the atmosphere is gradually increased. This is trapping more heat from earth resulting for the earth's temperature to rise. The phenomenon known as the ***global warming***. Climate change, on the other hand, refers to the effect of global warming to the winds and ocean currents in ways that can cool some areas and warm others.

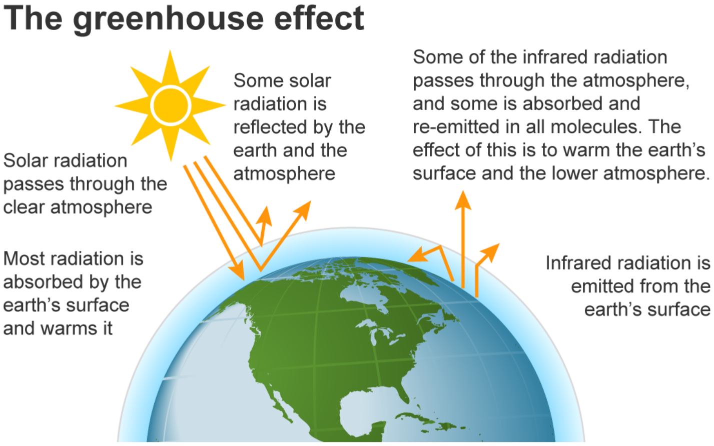


Figure 14: The Greenhouse Effect Image source: www.eia.gov

The greenhouse effect is primarily due to the augmented emissions of CO_2, NO_x, water vapor and other greenhouse gases into the atmosphere. Water vapor is the largest contributor to greenhouse effect because it absorbs infrared radiation. It helps in the maintenance of atmospheric temperature during night time when the earth's surface is emitting radiation into space. The second major contributor is the carbon dioxide due to the increase in energy production. Although carbon dioxide is being absorbed by the oceans and is being used by plants during photosynthesis, its generation is much faster than being absorbed or used. Another main contributor is the methane production due to the increasing demand on rice production (methane is produced in rice pads) and the intensive livestock breeding. Other greenhouse gases include chlorinated alkyl compounds (such as CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs).

Photochemical Smog Formation

Photochemical smog is a consequence of photochemical reactions based on primary pollutants discharged into the atmosphere. Smog has many deleterious effects on human health as well as on plants and materials. Nitrogen oxides and hydrocarbons emitted from vehicles with sunlight and oxygen produce pungent nitrogen dioxide and toxic ozone.

$$N_2 + O_2 \rightarrow 2NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + hv \rightarrow NO + O\cdot$$

$$O\cdot + O_2 \rightarrow O_3$$

$$O_3 + NO\cdot \leftrightarrow NO_2 + O_2$$

NO and NO2 can also react with other free radicals that come from hydrocarbon emission after reacting with strong oxidizers.

The Stratospheric Ozone Destruction

Stratospheric ozone protects life on the surface of the Earth by screening harmful UV radiation coming from the sun through a photodissociation mechanism.

$$O_3 + hv \rightarrow O_2 + O\cdot$$

$$O\cdot + O_2 \rightarrow O_3$$

However, anthropogenic generated chlorine and bromine compounds in the atmosphere are responsible in the decrease in the ozone concentration in the stratosphere. Chlorine and bromine compounds are converted into it more active forms – free radicals.

$$Cl_2 + hv \rightarrow 2Cl\cdot$$

$$ClO\cdot + BrO\cdot \rightarrow Br\cdot + Cl\cdot + O_2$$

$$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$$

$$Br\cdot + O_3 \rightarrow BrO\cdot + O_2$$

$$2O_3 \rightarrow 3O_2$$

With this, Montreal Protocol was established with numerous signatories around the world. It has an objective of saving the ozone layer from destruction by abandoning the use of ozone depleting substances.

The Acid Rain

Under normal conditions, the pH of rain is slightly acidic at 5.7 due to the dissociation of dissolved carbon dioxide in water:

$$CO_2 + H_2O \rightarrow HCO_3{}^- + H^+$$

However, in polluted environments, oxides of sulfur and nitrogen are also present which when dissolved in rain droplets, its pH goes below 5.7. This is how the formation of acid rain occurs.

Sulfur dioxide (SO_2) come from the combustion of sulfur-containing fossil fuels. It is oxidized in the atmosphere to form sulfur trioxide (SO_3) which reacts with water to form sulfuric acid:

$$SO_2 + O\cdot \rightarrow SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$H_2SO_4 \rightarrow SO_4{}^- + 2H^+$$

On the other hand, nitrogen oxides form due to the presence of nitrogen and oxygen gases in air. These two goes on a series of chemical reactions to produce nitric acid, another component of acid rain.

$$N_2 + O_2 \rightarrow 2NO\cdot$$

$$2NO\cdot + O_2 \rightarrow 2NO_2\cdot$$

$$3NO_2\cdot + H_2O \rightarrow 2HNO_3 + NO\cdot$$

$$HNO_3 \rightarrow NO_3^- + H^+$$

Acid rain oxidizes materials such as copper and iron. They also cause deterioration of marble and other carbonate materials due to the decomposition reaction:

$$CaCO_3 + 2H^+ \rightarrow CO_2 + H_2O + Ca^{2+}$$

Volcanic eruptions are natural sources of SOx, while lightnings are natural sources of NOx and ozone. Combustion processes remain as the top anthropogenic sources of SOx and NOx.

Activities and Assessment:

1) Enumerate the ten groups of air pollutants and discuss their respective sources and effects.
2) How does the incomplete internal engine combustion add to air pollution?
3) Differentiate greenhouse effect, global warming and climate change. How are the three related to each other?
4) How does human activities contribute to photochemical smog formation, stratospheric ozone destruction and acid rain formation?
5) Suggest ways of how are you going to contribute to climate change, minimization of photochemical smog formation, destruction of ozone layer and acid rain occurrences. Cite one for each.

LESSON 11: CHEMISTRY OF THE HYDROSPHERE
UNIT 1: The Composition of the Hydrosphere

Introduction:

The hydrosphere is one of the geological spheres that makes up the earth. It is composed of the different water bodies that are found on the surface and deep below the earth, including the water that is found in the atmosphere. In this lesson, the major composition of the hydrosphere – water - is explored. An overview on the importance of water and the interrelationship between its composition, structure and properties are presented. Also, a deeper discussion on the water cycle and global water distribution are also included.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1) Describe the importance of water.
2) Explain the properties of water with respect to its composition and structure.
3) Discuss the different processes within the hydrological cycle.
4) Label the different water bodies with their approximate global distribution.

Course Materials:

The Water Molecule

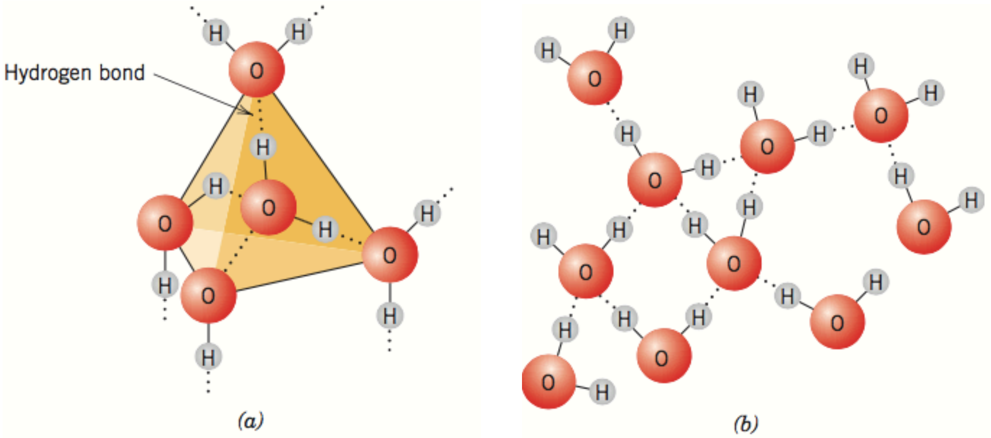


Figure 15: Water molecules in (a) solid form and (b) in liquid form. Image source: *Callister Jr., W. (2007) Material Science and Engineering An Introduction, John Wiley & Sons, Inc., USA*

Water serves as the home to many aquatic organisms. It boosts growth of plants. It also provides nutrients and minerals for the sustenance of physical life. With this, it is considered as an essential nutrient that we cannot live without.
The importance of water is due to it renowned properties. It is an excellent solvent, has a high surface tension and exists in wide range of temperature in its liquid form. These properties is due to its composition and structure.
Water molecules is made up of one hydrogen and two oxygen atoms forming two O-H bonds leaving two unpaired electrons on the oxygen. The distribution of forces among the elements

results to its bent molecular structure. In addition, the oxygen atoms in the water molecule have high electronegativity which makes them attract the O-H bond creating strong dipoles that attract each other and form new bonds known as the hydrogen bond. The hydrogen bonds among the water molecules is what maintain a strong adhesion among the molecules.

The Hydrological Cycle

The hydrological cycle involves the physical changes water undergoes as it continuously move above, on and below the surface of the earth. It is also known as the water cycle. As it goes through the cycle, it serves as a reagent in the chemical transformations of matter and as a transport medium for compounds to the different parts of the earth.

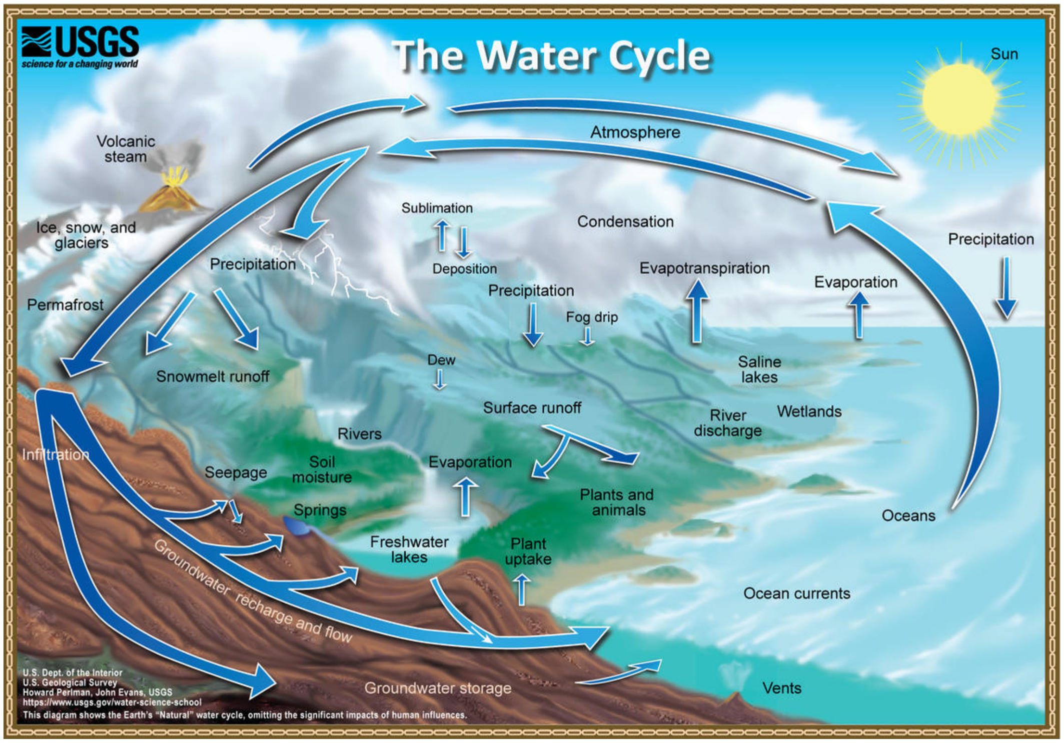


Figure 16: The Hydrological Cycle. Image source www.usgs.gov.

a) Evaporation

Evaporation is the process wherein the liquid water changes into gas at ambient temperature. The heating of bodies of water and of lands by the sun causes evaporation of some of its waters into the air.

b) Sublimation

Evaporation is not the only source of water vapor in air. Some of the water components of ice and snow sublimes to water vapor. Sublimation is the process wherein the solid water changes into gas.

c) Evapotranspiration

Apart from evaporation and sublimation, evapotranspiration also contributes to the amount of water vapor that enters the atmosphere. Evapotranspiration is a combination of evaporation and transpiration. Transpiration is the process by which plants takes water from the soil through its roots and later released through its leaves. The water that is released is further evaporated into the air.

d) Condensation

The water vapor resulting from the processes of evaporation from the oceans, sublimations from ice and snows and transpiration from plants are carried up into the atmosphere by rising air currents. When the vapor reaches the air of cooler temperature, it transforms into clouds through the condensation which is the process wherein water vapor changes into liquid.

e) Precipitation

The clouds are moved by air currents, collide, grow and fall out as precipitation which is the process wherein liquid or frozen water in the atmosphere goes back to earth in the form of rain, snow or sleet. Most precipitation falls back to the land, oceans and other bodies of water.

f) Runoff

Runoff is the process when water runs over the surface of the earth. The snow precipitates are accumulated as ice caps and glaciers but some of them melts wherein the melted water flows as a snowmelt over lands as snowmelt runoff. Some of the precipitation flows over the ground as surface runoff. Portions of the runoffs goes to the rivers and oceans. Some of the precipitate go through groundwater seepage and later stored as freshwater in lakes.

g) Infiltration

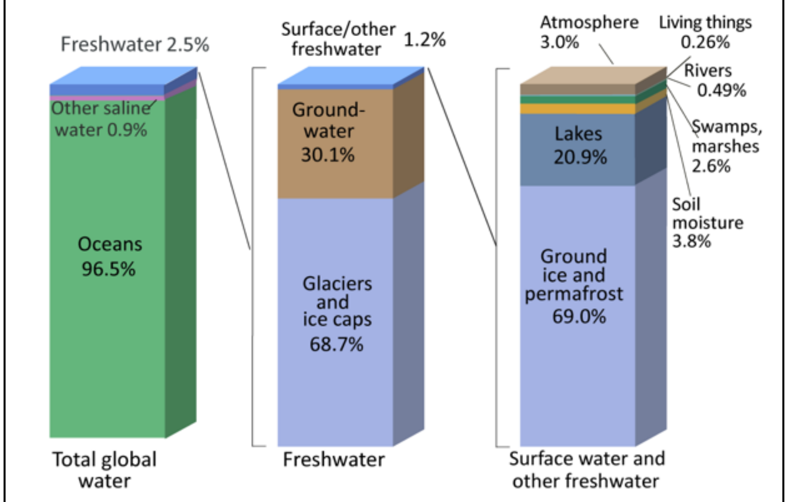
Not all runoffs goes back to the hydrosphere, absorbed by plant or get evaporated because much of the water soaks deep into the soil through the process of infiltration. Some of the water infiltrates deep into the ground to replenish the ground water table and aquifers. Some stays close to the land surface and seeps back into the surface as groundwater discharge and freshwater springs.

Global Water Distribution

Estimate of Global Water Distribution	**Volume (1000 km3)**	**Percent of Total Water**
Oceans, Seas, and Bays	1,338,000	96.5
Ice Caps, Glaciers, and Permanent Snow	24,064	1.74
Groundwater	23,400	1.7
Fresh	(10,530)	(0.76)
Saline	(12,870)	(0.94)
Soil Moisture	16.5	0.001
Ground Ice and Permafrost	300	0.022
Lakes	176.4	0.013
Fresh	(91.00)	(0.01)
Saline	(85.40)	(0.01)
Atmosphere	12.9	0.001
Swamp Water	11.47	0.0008
Rivers	2.12	0.0002
Biological Water	1.12	0.0001
Total	**1,385,984**	**100**

Source: Gleick, P. H., 1996: Water resources. In *Encyclopedia of Climate and Weather,* ed. by S. H. Schneider, Oxford University Press, New York, vol. 2, pp.817-823.

Where is Earth's Water?



Source: Igor Shiklomanov's chapter "World fresh water resources" in Peter H. Gleick (editor), 1993, Water in Crisis: A Guide to the World's Fresh Water Resources. (Numbers are rounded).

Activities and Assessment:

1) Why is water important?
2) How are the properties of water related to its composition of having two atoms of hydrogen and one atom of oxygen?
3) How does the hydrological cycle work?

LESSON 11: CHEMISTRY OF THE HYDROSPHERE
UNIT 2: The Chemistry of Natural Waters

Introduction:

In the previous section, the relationship of the structure and composition of water to its function were discussed. A more extensive discussion on how the global water maintains its existence through the global water cycle was also undertaken. In this section, the different classifications of natural water are examined including the processes on how they were formed and the different factors that affect their quality.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Differentiate the classifications of natural waters according to their sources.
2. Describe how the different natural waters are formed.
3. Discuss how the different factors affect the water quality.

Course Materials:

Natural waters are comprised of rainwater, surface water, groundwater, sweater and saline water.

1) Rainwater

Rainwater comes from the evaporation, condensation and precipitation processes in the water cycle. It takes 8 – 10 days for the water in the atmosphere before it precipitates as rain. The rainwater composition depends on the zone of the origin of the clouds that carried it, the composition of the winds that carried them to the precipitation cite and on the composition of the atmosphere at the precipitation zone.

The pH of the rainwater depends on the compounds found in the atmosphere. The presence of carbon dioxide (CO_2) makes it slightly acidic. The sulfate concentration also lowers the pH of rainwater. Compounds such as SO_2 and NO_2 undergoes oxidation and dissolution to produce sulfuric and nitric acid, respectively. This is the cause of acid deposition such as ***acid rain***. Moreover, the sulfuric and nitric acids formed can further react to ammonium ions from the dissolution of ammonia to produce ammonium salts.

The salinity content of rainwater depends on the amount of salt particles that are suspended in air when the rain falls. These salt particles are results of evaporated marine-generated aerosols and gases that were released from the sea surface.

2) Surface water

Surface water is formed when the precipitation rate exceeds the infiltration rate. The excess water flows as runoff and gets to streams, rivers, ponds, lakes, swamps, marshes and springs. The composition of surface waters depends on the processes that takes place in the geographic zone such as weathering, precipitation and eutrophication.

In zones where soil weathering prevails over rainfall, the surface waters has a moderate ionic strength brought by the presence of calcium ions, bicarbonate ions and silicates which are the common minerals resulting from weathering. If vegetation and animal excretes are abundant in an area, the presence of organic and inorganic matters are dominant as particulate solids and dissolved organic matter. Places with surface waters having rich organic compounds are also abundant with ammonia, nitrates and orthophosphates due to the rich aquatic fauna and flora in the area.

In places where rainfall predominates over soil weathering, the lower concentration of total dissolved salts in the surface waters has a low ionic strength. However, the concentration of ions in surface waters is also affected by the amount of ions present in the atmosphere that are washed by rainwater such as sodium ions, magnesium ions, chloride ions and sulfate ions.

Another important process that affects the composition of surface water specifically rivers and lakes is ***eutrophication***. It is a condition when a body of water is enriched with excessive nutrients from surface runoff and stimulates growth of plants. This results to a decrease in the concentration of dissolved oxygen in the body of water causing death to the aquatic species living in it.

3) Groundwater

Groundwater is the accumulated water that fills the water table and the aquifers that came from precipitation and was infiltrated through the soil. The water table is below the surface of the ground where water can be found. The aquifers, on the other hand, is made up of permeable rocks that holds a large reservoir of water that can easily be transmitted into springs are wells. Groundwater is also the water in voids and spaces between soil, sand, gravel, clay silt and rocks.

The quality of ground water is good enough for human use and consumption as it contains minerals and nutrients that are essential for body functions. The nutrients and minerals that the groundwater contains is dependent on the composition of the soil and rocks that it penetrates on its way to the water table and aquifers. The most common ions that are naturally occurring in groundwaters are magnesium ions, calcium ions, potassium ions, sodium ions, ferric ions, ferrous ions, chloride ions and percarbonate ions. Normally, the groundwater has a pH level of 6.5 to 8.

4) Seawater

The seawater is composed of all waters that are leading to the seas and the oceans and it comprises 97% of the waters in the whole planet Earth. It is the home of thousands of aquatic species whose lives depend on the composition of the saltwater. Aerobic biological processes is supported in seawaters due to the presence of high amounts of dissolved oxygen resulting from gas transfer and dissolution promoted by strong mixing process. On the other hand, anaerobic biological processes are supported in the deeper parts of the ocean where lower dissolved oxygen levels are available.

Most of all minerals and nutrients that are found in seawater comes from different sources that were carried by the waters leading to its place. Seawater has high in salinity (mainly as NaCl) and in dissolved solids contents. ***Salinity*** is defined as the amount of dissolved solids per gram of seawater. Studies show that the major ions present in seawater are sodium, potassium, calcium, magnesium and the chloride ion. These minerals along with the intense surface and current movements of the seawater affects the different process occurring therein including the removal of the minerals.

5) Brackish/Saline Water

When the salt content of the water is greater than the fresh water but lower than that of the seawater, it is categorized as brackish or saline water. It has an average salt content of 0.5 to 30 g/L. Saline waters are usually classified according to their salinity to check their possibility of being used in irrigation systems. This is because high salt concentration may be toxic to plants or accumulate in plants and later place their consumers at risk.

Activities and Assessment:

1. What makes rainwater acidic?
2. How does weathering, precipitation and eutrophication affect the quality of surface waters?
3. What makes groundwater suitable for human consumption?

LESSON 11 : CHEMISTRY OF THE HYDROSPHERE
UNIT 3: Water Pollution, Sources and Effects

Introduction:

The hydrosphere is one of the important spheres of the earth that we need to take care of. We have known how important it is for our survival; therefore, it is important for us to understand how it will get destroyed so that we know how to prevent it. This part of the lesson discusses the effects of the different pollutants in the hydrosphere.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1) Describe the different sources of water pollutants.
2) Discuss the impacts of each of the pollutants to the bodies of water and the organisms living in them.

Course Materials:

The common water pollutants and their corresponding effects are as follows:

1) Oxygen-Demanding Materials

   Oxygen-demanding materials are compounds in water bodies that consume dissolved molecular oxygen. They can either be biodegradable organic or inorganic compounds. These materials are can come from human wastes and food residues that are dumped into water bodies.

   The amount of oxygen-demanding compounds present in water can be measured in two (2) ways: Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD).

   COD measures of the amount of the amount of molecular oxygen required to achieve a complete chemical oxidation of a sewage sample using a strong oxidizing agent mixed with a water sample and then heated to 150°C for two hours. The difference on the amount of oxidizing agent before and after the oxidation process is recorded as COD in mg/ L.

   BOD, on the other hand, is used when the oxidation process is carried by microorganisms instead of strong oxidizing agent. In a BOD_5 test, microorganisms are introduced to a water sample where they oxidize the organic and inorganic compounds in the dark at 20°C over a period of 5 days.

   High COD and BOD values mean high organic content of the water sample. Discharging water with high COD and BOD values results to a reduction of dissolved oxygen in water and may pose threat to the aquatic organisms that require it for respiration.

2) Nutrients

Of all the nutrients available, phosphorous and nitrogen are of primary concern with respect to the water quality because they are essential to the growth of living organism. Their presence in waters supports the natural food chain; however, when excessive, some of the organisms proliferate at the expense of others.

Moreover, due to excessive nutrient concentrations, bodies of water becomes shallower and more productive. A process called ***eutrophication***. This may promote algal growth that eventually result in higher supply of food for higher organisms. With higher fish population, water quality will suffer due to algal death and decomposition.

Sources of nutrients are phosphorous-based detergents, fertilizers and food-processing wastes.

3) Pathogenic Organisms

Pathogens are disease-causing bacteria, viruses and other parasitic organisms that are present in waters usually from untreated sewage. They can contaminate drinking, swimming and bathing waters and food. These medium can be used by the pathogens to access individuals and cause the diseases such as typhoid fever, cholera, diarrhea and dysentery.

4) Suspended Solids

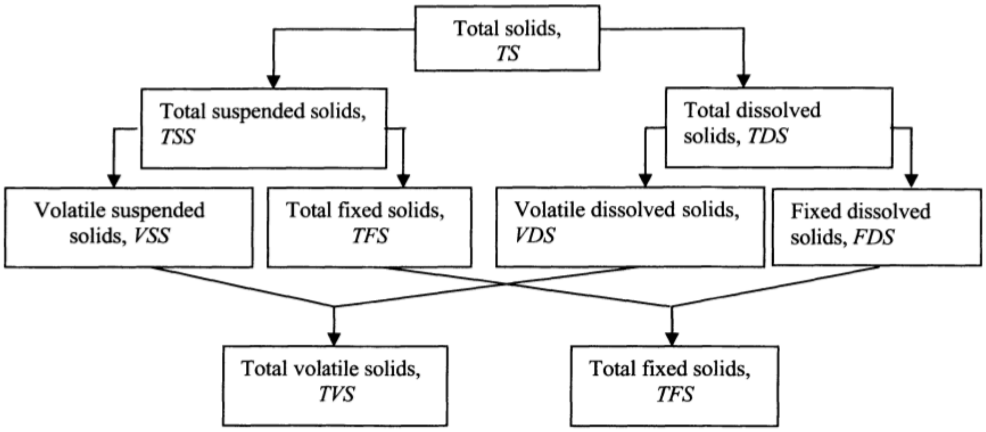


Figure 17: Classifications of Solids in Water. Image Source Ibanez, J.G., et. al. (2007) ***Environmental Chemistry Fundamentals***, Springer Science+Business Media, LLC, New York, USA

Total solids (TS) are those that are obtained by evaporating a sample wastewater to dryness at 103 to 105°C. These TS undergo filtration: the filtered ones are called as *Total Suspended Solids (TSS)* and those that were dissolved and became part of the filtrate are the *Total Dissolved Solids (TDS).* When the TS are subjected to ignition at 500°C: the residue is known as the *Total Fixed Solids (TFS)*, while those that were volatilized are the Total *Volatile Solids (TVS).*

Some of the pathogenic organisms may be encased in the solids which serves as their protection against disinfection. With this, the amount of suspended solids present in water became a measure of a waste treatment facility's efficiency. It can be determined by means of turbidity - the measure of the light scattering properties of water. The higher the content of suspended solids, the more polluted the water is.

5) Oil and Grease Spills

Oil and grease spills are products of accidents, lack of maintenance and neglectfulness from machineries. In addition to being displeasing to the eye, oil and grease spills has negative impact on the environment and on the living species in the area because oil and grease are toxic and carcinogenic. Moreover, oil emulsions block the entrance of light into the bodies of water resulting in a decrease of biological activities.

6) Metallic and Metalloid Compounds

The presence of metallic and metalloid compounds can be attributed to widespread human activities such as mining ang smelting. These compounds can damage deep-rooted plants and contaminate groundwater. They are in some of their forms are toxic and hazardous both to humans and other organisms. In addition, they also increase the water turbidity and coloration, stain materials in contact to it and gives the water a bad taste.

7) Radionuclides

Mishandled radionuclides are toxic to human health. Most of them came from nuclear facilities and improper disposal of medical applications.

8) Detergent and Nutrient Enrichment

As discussed earlier, nutrients can cause eutrophication which results in death of algae, microbial degradation and decrease in dissolve oxygen thereby lowers the life-sustaining ability of the water. In addition, algae impedes the access of light into the water affecting the natural photosynthesis of organisms therein.

9) Salts

Salt coming from industries may affect the quality of water such that it is no longer useful for public water supply and irrigation. High salt concentration damages crops and causes soil poisoning.

10) Heat

Heat is not considered as pollutant but it produces problems at their disposal to bodies of waters. High water temperature kills some of the water species and it also increase the rate of dissolved oxygen depletion.

11) Others

Large plastics resemble food of larder organisms in the bodies of water. On the other hand, plastic debris may be broken down into smaller fragments which may threat the lives of the organisms that happen to ingest them.

Activities and Assessments:

1) What is the difference between COD and BOD?
2) How does high values of COD and BOD affect the lives of aquatic organisms?
3) How does eutrophication takes place? How does it affect water quality?
4) What are the impacts of oil and grease spills in bodies of water?
5) Explain how plastics of various sizes affect organisms living in bodies of waters.

LESSON 12: CHEMISTRY OF THE LITHOSPHERE
UNIT 1: The Structure and Composition of the Earth

Introduction:

The field of chemistry discusses the structures and compositions of different substances including the changes that they undergo as a result of the various interactions among the elements they are composed of.

In this particular lesson, the overview on the structure and composition of the huge spherical land structure beneath the place that we call "home" is discussed. The composition of the different layers of the earth is presented and how they affect their structure and properties.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Differentiate the structures and composition of the solid earth.
2. Discuss the composition and the importance of the lithosphere.

Course Materials:

The Four Layers of the Earth

The earth is made up four (4) spherical layers namely inner core, outer core, mantle and crust as shown in Figure 1.

The center of the earth is the core with a diameter of approximately 25000 km. It is believed that the high temperature, earth's rotation and its density caused iron to move to the center of the earth. As it moved to that direction, the iron came in contact with siderophiles (iron-loving elements) such as nickel. This is the reason why the earth's core is made up of iron and nickel predominantly present in their reduced form.

a) The inner core

   The *inner core* which is like a rotating solid metal ball that is made of iron and nickel with a diameter of approximately 2440 km.

b) The outer core

The *outer core* is also made up iron and nickel but in the liquid form. This part of the earth is what generates the electromagnetic field of the earth as a result of the turbulent current of the earth is heated through the radioactive decay of uranium and thorium which causes turbulent current which in turn generates the electromagnetic field of the earth.

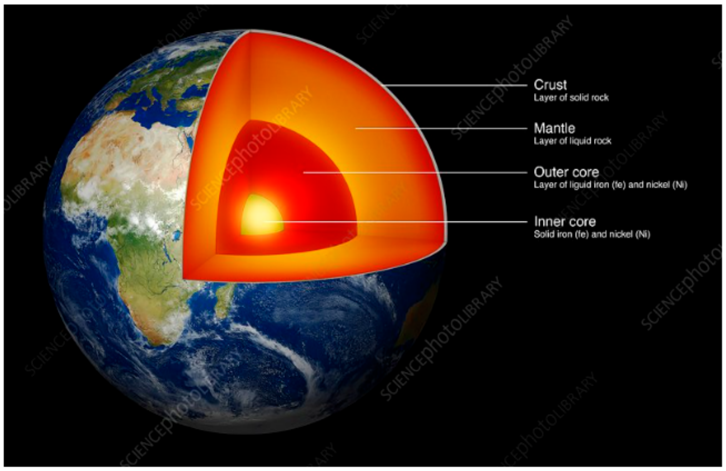


Figure 18: The layers of earth. Image from www.sciencephoto.com

d) The mantle

The *mantle* surrounds the core and it has a thickness of approximately 2900 km. It is made up of high-density silicates of magnesium and iron and is further divided into three layers: the lower mantle, the transition and the upper mantle. The lower mantle contains water that is believed to have a greater amount than that of the oceans at the surface. These water is contained within the magnesium and calcium crystals that it is composed of.

d) The crust

The *crust* surrounds the mantle and is considered as the thinnest among the layers of the earth: it is approximately 8 km from the bottom of the oceans (oceanic crust) and an average of 40 km under the continents (continental crust). It is primarily made up of oxygenated silica and aluminum. The components of the earth's crust is predominantly in their oxidized form. The upper part of the crust is made up of gigantic broken pieces known as the tectonic plates that move slowly. The cause of movement, however, is not yet fully understood until now.

The Lithosphere

The *lithosphere* is the solid outer part of the earth. It is made up of the upper mantle and the crust. It has two types: the oceanic lithosphere and the continental lithosphere.
The lithosphere defines a great deal on the kind of life we have. It is believed that the uppermost part of the mantle is what the tectonic plates ride upon. The thermal energy present from the mantle is believed to cause the movements of the tectonic plates which defines territories and geographical landmarks. Moreover, the lithosphere is where the process of weathering occurs. Weathering is the one of the factors that determines the formation of our landscapes and the distribution of minerals and nutrients among soils. It is the soil that the growth of living organism are highly dependent on.

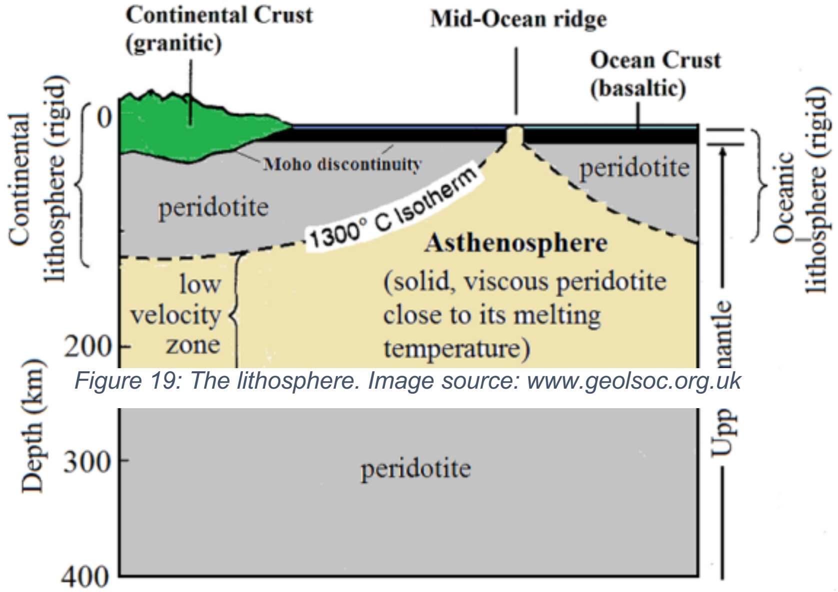


Figure 19: The lithosphere. Image source: www.geolsoc.org.uk

Activities and Assessment:

1. What are the three layers of the earth and their respective compositions?
2. What comprises the lithosphere?
3. Why is the lithosphere important?

LESSON 12: CHEMISTRY OF THE LITHOSPHERE
UNIT 2: Rock Classifications and the Rock Cycle

Introduction:

The lithosphere is where most of our lives are spent. Rocks and minerals are very important part of the lithosphere as it provides habitant to numerous living organisms. Whatever changes they undergo will result to changes in the ecosystem and the lives that depend on it. A better understanding on how these rocks were formed will give us insights on how to keep the balance going. In this lesson, we are to have an overview on the different classifications of rocks, their chemical compositions and the processes they undergo.

Learning Objectives:

After successful completion of this lesson, the students are expected to:
1. Differentiate the three different classifications of rocks and their sub-classifications.
2. Discuss the processes on how the different rock classifications are formed.
3. Describe how the rock cycle works.

Course Materials:

Rock Classifications

The continental crust is usually made up of different kinds of rocks which are classified as (1) igneous, (2) sedimentary and (3) metamorphic.

a. Igneous rocks

   Igneous rocks are formed when hot materials cool and solidify. Its primary content is silica dioxide (SiO_2) with their percent content as the basis on how they are classified. However, SiO_2 does not exist on the rock in the said form but as a part of a more complex structure. Studies also show that in igneous rocks, as the SiO_2 content decreases, the magnesium oxides (MgO) or calcium oxides (CaO) content increases. It is the SiO_2/MgO ratio found in the rock that serves as the basis for their classifications. For *granite*, the ratio is 72.0/0.5; for *diorite*, the ratio is 54.5/3.8; for *basalt*, the ratio is 48.4/8.1; and for *peridotite*, the ratio is 43.5/34.0. In addition, the quartz-rich rocks are called *felsic* or *silicic* while basic rocks are called *mafic*.

   There are two types of igneous rocks which are classified according to the mechanism on who they were formed. *The intrusive (plutonic) igneous rocks* are those that are formed inside the earth while the *extrusive (volcanic) igneous rocks* are those that are formed outside the earth.

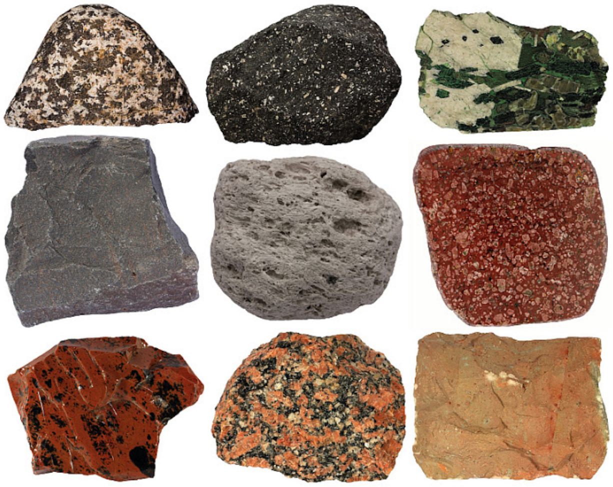


Figure 20: Samples of Igneous Rocks. Image source: www.sandatlas.org

b) Sedimentary Rocks

Sedimentary rocks are results of erosion and from the interaction of igneous and sedimentary rocks with different factors in the environment. These rocks have lower silica contents compared to the igneous and metamorphic counterparts. Their SiO_2/CaO content ratio determines whether its classification. Limestones have a ratio of 8.2/40.5 while sandstones have 74.3/34.9.

Sedimentary rocks have three types: (1) clastic, (2) organic and (3) chemical. *Clastic sedimentary rocks* are those that are formed from pieces of other rock materials while *organic sedimentary rocks* are those that are formed from biological materials that were compressed into rocks.

Clastic and organic sedimentary rocks are formed through weathering and erosion. Exposed rocks are broken down into segments through *weathering* and are transferred to other locations through *erosion*. At the new location, the segments are collected until it forms a new solid rock formation.

Chemical sedimentary rocks are those that are form through the process of *chemical precipitation*. This occurs when the minerals in the rocks are dissolved by water and transfer elsewhere. The dissolved minerals are precipitated during the evaporation process.

Figure 21: Samples of Sedimentary Rocks. Image Source www.sandatlas.org

c) Metamorphic rocks

Metamorphism is the process on which rocks undergo physical and chemical alterations due to their exposure to high temperature and pressure. This is how *metamorphic rocks* are formed. There are two types of metamorphic rocks: (1) foliated and (2) non-foliated. The *foliated metamorphic rocks* has evidences that it underwent the process of foliating. *Foliating* is the formation of aligned elongated or platy minerals perpendicular to the pressure of force exerted. *Non-foliated metamorphic rocks* are formed the same way but with the absence of foliation. They can also be formed by undergoing the process of metamorphism when they come in contact with magma.

Figure 22: Samples of Metamorphic Rocks. Image Source www.sandatlas.org

The Rock Cycle

The different classifications of rocks described above are formed through different physical processes that are part of the rock cycle.

The contents of a rock are broken down into pieces and are transported to other locations where they are collected. This process forms the sedimentary rock which goes through changes under high temperature and pressure forming the metamorphic rock. Further changes may take place to transform to an igneous rock from which the contents are broken down to start a new cycle.

However, it should be noted that a rock has two routes that may undergo in the rock cycle. The sedimentary rock may undergo either the same cycle of wreathing and erosion that it went through or the process of metamorphosis to form the metamorphic rock.

The metamorphic rock may undergo the cycle of weathering and erosion the sedimentary rock underwent or be formed into igneous rocks through the process of metamorphosis.
The igneous rock may undergo metamorphosis to form back to the metamorphic rock or the weathering and erosion processes that the rock contents need to undergo to complete the cycle.

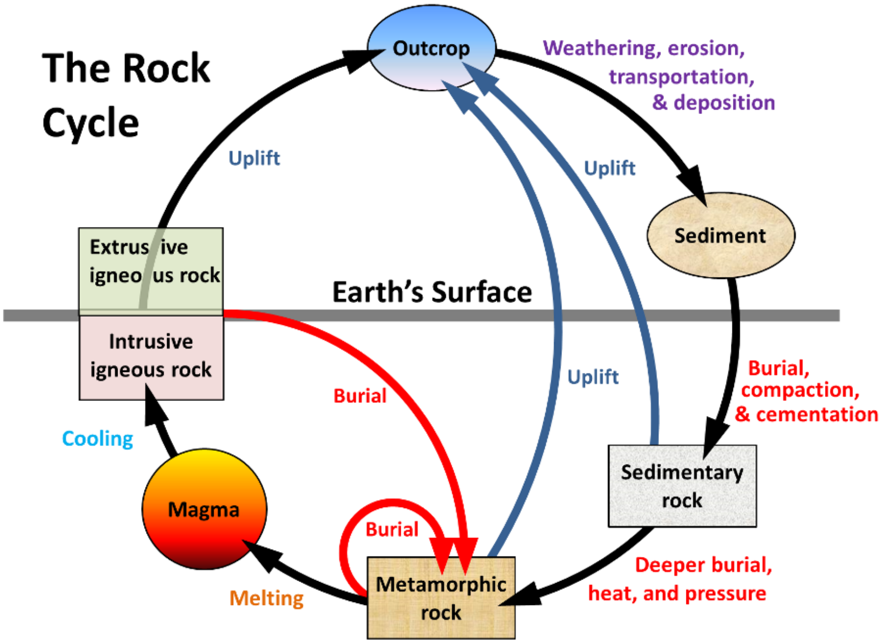


Figure 23: The Rock Cycle. Image Source opentextbc.ca

Activities and Assessment:

1. What are the three classification of rocks?
2. What are the two types of igneous rocks and how do they differ?
3. What are the three types of sedimentary rocks and how did they differ?
4. What are the two types of metamorphic rocks?
5. Explain how the following processes takes place: (a) weathering, (b) erosion, (c) chemical precipitation, (d) metamorphose and (e) foliating.
6. Briefly describe how the rock cycle takes place.

LESSON 12: CHEMISTRY OF THE LITHOSPHERE
UNIT 3: The Process of Weathering

Introduction:

Weathering is the process of breaking down of rocks into smaller pieces that can be done through physical or chemical changes. It is an importance process that occurs in the lithosphere as the creation of landscapes is highly dependent on it. Moreover, weathering is also an important of soil formation which we are highly dependent on. In this lesson, the different methods on how weathering occurs is discussed to help the student understand the underlying chemistry principles behind landscapes formation and soil formation.

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Define the process of weathering and its importance.
2. Differentiate the three classifications weathering.
3. Describe how the different mechanical weathering processes take place.
4. Describe how the different chemical weathering processes take place.

Course Materials:

Weathering

Weathering is the process that rocks undergo where they are broken down into pieces or their mineral contents are dissolved. Weathering followed by the erosion processes has a great contribution on how different landscapes on the planet are changed.

Weathering is also considered as one of first processes in the formation of soil. The minerals and nutrients that are found in soils determines the kind of plants that can survive on it. The minerals and nutrients present in soils is dependent on the type of weathering that occurs in the place.
The weathering process can be characterized as mechanical, chemical or biological in nature.

Mechanical Weathering

Mechanical weathering is also known as *physical weathering* wherein rocks are broken down into pieces without altering their chemical composition. It can be classified into two: (1) those that forces the rock apart like a wedge and (2) those that causes the rock to expand.

Mechanical Weathering by Wedging

a) Salt wedging

   When saltwater comes in contact with the rocks, they enter in it through the cracks and pores. The salt is left behind after evaporation. These salt crystals grow that causes the rocks to fall apart. This process is known as *haloclasty or salt wedging.*

b) Frost wedging

Water can get into the rocks through rocks and crevices. The water freezes when the temperature drops which cause it to expand. This water expansion causes the cracks to widen. When the ice melts, the liquid water carries out the tiny fragments. This process is known as *frost weathering* or *cryofracturing*. Moreover, the contact of water with the rocks may also cause abrasion as the water washes away some of the particles from the rocks.

c) Root wedging

The growths of plant roots causes damage on the rocks as they widen the cracks and eventually breaks them into pieces. This process is known as root wedging.

Mechanical Weathering by Expansion

a) Thermal expansion and contraction

The changing temperature also causes rock destruction as it undergoes thermal stress. The rocks expands when heated, contracts when cooled. As the rocks undergo this *expansion-contraction cycle*, it weakens and cracks are produced.

b) Exfoliation

Changing pressures can also cause rock expansion which makes the rocks vulnerable to breakage. Exfoliation occurs when the outer layer of rocks break off in slabs or sheets as a result of the outer layer's expansion due to change in pressure.

c) Impacts and abrasions

Wind. The wind carries particles that has the capability to cause abrasion on the rocks such as solid particulate matters.

Earthquakes. The large magnitude of forces caused by earthquakes have direct effects on the change on the structure of rocks. As these forces shake the rocks, their structural integrity is compromised that may lead the rocks to be broken down into smaller pieces.

Biological activities. Some animals dig and squash rocks which cause them to deteriorate and crush.

Chemical Weathering

Chemical weathering occurs when the chemical composition of the rocks were changed by virtue of chemical reactions. The following are the common chemical processes that rocks undergo:

a. Dissolution

Dissolution occurs when a component of a rock reacts to a substance such that the resulting product is a soluble compound. With this, when the compound interacts with a solute, it is completely dissolved leaving no residues behind. Dissolution is a major process in the creation of sinkholes.

One form of dissolution in rocks is c*arbonation.* It is a process wherein the carbon dioxide occurring in air combines with water to produce carbonic acid, H_2CO_3. This carbonic acid reacts with other carbonate components of the rock such as calcium carbonate ($CaCO_3$) which is broken down further into its constituents calcium ion, water and carbon dioxide. The calcium iron can be part of another rock, while the water and carbon dioxide will cycle back to nature. The process of dissolution is what occurs to the chemical weathering of limestones, dolomites and metamorphic rock marble.

$$CO_2 + H_2O \rightarrow H_2CO_3 \leftrightarrow 2H^+ + {CO_3}^-$$

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2H_2O + CO_2$$

Another means of dissolution is *acidification* such as what happens in the destruction of rocks caused by acid rain:

$$CaCO_3 + H_2S0_4 \leftrightarrow Ca^{2+} + {SO_4}^{2-} + CO_2 + H_2O$$

b. Oxidation

Oxidation is a process that involves the loss of electrons. In chemical weathering, oxidation usually occurs to rocks that contain iron and reacts with oxygen that is usually carried by water to form rust, Fe_2O_3. Since the structural composition of iron has a stronger than that of rust, the more rust is created, the weaker the rock becomes making it more vulnerable to breakage.

The process of oxidation is what makes a basalt rock look reddish due to the production of hematite, Fe_2O_3 from its iron-rich mineral content olivine Fe_2SiO_4. The olivine reacts with carbonic acid (H_2CO_3) and produces dissolved iron, bicarbonate ion and silicic acid. The dissolve iron reacts with the oxygen dissolved in water with the presence bicarbonate to produce the hematite and carbonic acid.

$$Fe_2SiO_4 + 4H_2CO_3 \rightarrow 2Fe^{2+} + 4{HCO_3}^- + H_4SiO_4$$

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O + 4{HCO_3}^- \rightarrow Fe_2O_3 + 4H_2CO_3$$

c) Hydrolysis

Hydrolysis occurs in chemical weathering when a rock component reacts with water resulting to one or more new product(s). An example is the reaction of potassium feldspar ($KAlSi_3O_8$) with water to produce the clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$). Unlike in the process of dissolution, in hydrolysis, not all of the products are ions which can be dissolved. Feldspars and micas are weathered through hydrolysis.

$$2KAlSi_3O_8 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2K^+ + 2OH^-$$

d) Hydration

Hydration occurs when water molecule is added as an integral part of the molecular structure of the rock. An example is the hydration reaction of a mineral anhydrite with water to produce gypsum.

$$CaSO_4 + H_2O \rightarrow CaSO_4.H_2O$$

Biological Weathering

Biological weathering is when living organisms or once living organisms takes part on the process. Biological weathering can be part of either the mechanical or chemical weathering or both.

Assessment:

1. In your own words, what is weathering and why is it important?
2. What are the three classifications of weathering? How does one differ from the other?
3. Explain how the following processes takes place? (a) frost wedging (b) salt wedging, (c) root wedging, (d) expansion-contraction cycle, (e) abrasion and (f) exfoliation.
4. Indicate what is the specific chemical process that occurs in the following chemical changes: (a) pyrite to hematite; (b) feldspar to clay; (c) calcite to calcium and bicarbonate ions.

LESSON 12: CHEMISTRY OF THE LITHOSPHERE
UNIT 4: Soil Pollution, Sources and Effects

Introduction:

The lithosphere is important because it carries the soil that houses our vegetations that we are being feed from. Changes in the chemistry of the soil as effect of the weathering process also affects the soil characteristic; hence, the kind and quality of plants that it could carry. The introduction of pollutants into the lithosphere has an effect on the soil quality; hence, it is important for us to have an idea

Learning Objectives:

After successful completion of this lesson, the students are expected to:

1. Illustrate how pollutants lead to soil contamination.
2. Provide suggestions for better landfill usage.

Course Materials:

Soil contamination is caused by pollutants coming from the atmosphere and the hydrosphere. These pollutants may stay inactive, decompose or react with soil components through the process of oxidation, reduction, combination, precipitation, dissolution and metathesis. The product of the reaction may or may not be environment-friendly as compared to the starting material. On the other hand, if the pollutants are not to stay with the soil, they may end up in groundwater and may pose risk into its quality.

Common sources are as follows:

1) Aerially transported materials

   These are the pollutants that are being carried by the wind and precipitation (snow and rain). Smoke and dusts may carry organic and inorganic pollutants while gases such as sulfur dioxide and nitrogen oxides may damage vegetation. Atmospheric deposition also introduces heavy metals to soil which may lead to plant uptake.

2) Agricultural activities

   Fertilizers, soil additives, pesticides and herbicides are used by farmers in their crops to enhance yield. Sewage sludge are also used as fertilizer and it may contain heavy metals, nitrates, phosphates and detergents. These contain compounds, such as nitrates and phosphates, that may contaminate both the soil and groundwater.

3) Mining activities

   Sulfide from mining processes are oxidized when comes in contact to air. When these minerals come in contact with water, they form acidic aqueous solutions called as the ***acid mine drainage (AMD)***, as represented by the following equation (with Fe as the metal present):

$$FeS_2(s) + H_2O(l) + \frac{7}{2}O_2(g) \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+$$

The produced Fe^{2+} oxidizes to Fe^{3+} in air at low pH. Then the Fe^{3+} can either hydrolize to form insoluble Fe(III) hydroxide or act as a secondary oxidant to FeS_2:

$$FeS_2(s) + 14Fe^{3+} + 8H_2O(l) \rightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+$$

The AMD process promotes downstream deposition of insoluble Fe(III) species which may lead to soil contamination as a result to capillary rise and evaporation.

On the other hand, the production of protons and sulfate ions produce H_2SO_4 which has the capability to dissolve minerals resulting to an increase in the metal and nonmetal ion content and acidity level of bodies of water nearby which are active participants in the weathering process.

4) Landfill

Landfills usually involve solid wastes, industrial wastes and sewage sludge that lead to the contamination of land surfaces and neighboring surface waters.

Examples of solid wastes are waste paper, food, street wastes, plastic trash while that of industrial wastes are residual construction materials, pollution treatment wastes, safety items. Sewage sludge are those that are produced from waste water treatment facilities, commercial setting and storm-water runoff.

Activities and Assessment:

1) In your own words, discuss how does acid mine drainage form and how does it affect soil properties?
2) What are the common wastes that are being dumped into the landfills? How can you help in giving our landfills with longer “lives”?

CHEMISTRY FOR ENGINEERS - LECTURE
SUMMATIVE EXAMINATION

INSTRUCTIONS:

1. Read the questions carefully.
2. Write the corresponding CAPITAL letter of your answer on your assessment sheet
3. Answers should all be in BLUE or BLACK ink only. Answers written in pencil will not be corrected.
4. Answers with erasures will not be corrected.

__________1. Rhodium has an FCC crystal structure, an atomic radius of 0.1345 nm and atomic weight of 102.9 g/mol. Calculate the density of rhodium.

A. 6.20 g/cm^3
B. 30 g/cm^3
C. 12.4 g/cm^3
D. 24.82 g/cm^3
E. None of the above

__________2. Which of the following changes is NOT exothermic?
A. Melting copper
B. Combustion of butane
C. Condensing of steam
D. Freezing of water
E. All are exothermic processes

__________3. Consider the following thermodynamic properties:

i. Work done on a system
ii. Heat absorbed
iii. Entropy
iv. Enthalpy

Which of these properties are state function(s)?

A. i and ii only
B. i and iii only
C. i only
D. iii and iv only
E. all of the above

__________4. The combustion of methanol is described in the following equation:

$$CH_3OH(l) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

Calculate the enthalpy of combustion (∆Hc) of methanol using the values of standard enthalpies of formation (∆Hf).
A. - 1203 kJ/mol
B. - 441 kJ/mol
C. 727 kJ/mol
D. - 727 kJ/mol
E. None of the above

__________5. Which type of radiation is the least penetrating?

A. alpha
B. beta
C. gamma
D. x-ray
E. neutron

__________6. Electron sea exists in

A. Polar bond
B. Ionic bond
C. Covalent bond
D. Metallic bond
E. Hydrogen bond

__________7. A gradual increase in the overall temperature of the earth's atmosphere generally attributed to the greenhouse effect caused by increased levels of carbon dioxide, chlorofluorocarbons, and other pollutants.

A. Ozone depletion
B. Photochemical smog
C. Greenhouse effect
D. Eutrophication
E. Global warming

__________8. The equation that relates enthalpy, temperature and entropy.

A. Hess' Law
B. Gibbs Free Energy
C. Second Law of Thermodynamics
D. First Law of Thermodynamics
E. Nernst Equation

__________9. Which column elements are combined to make compound semiconductors?

A. First and fourth
B. Fifth and sixth
C. Second and fourth
D. Third and fifth
E. All of the above

__________10. In the standard notation for a voltaic cell, the double vertical line "||" represents:

A. a phase boundary
B. gas electrode
C. a wire (metal) connection
D. a salt bridge
E. a standard hydrogen electrode

__________11. When does the atomic number always change?

A. After alpha decay and gamma decay
B. After beta decay and gamma decay
C. After beta decay and alpha decay
D. After positron emission and gamma decay

__________12. A positron has a mass number of _____, a charge of _____, and a mass equal to that of a(an) _____.

A. 0, 1+, proton
B. 1, 2+, proton
C. 0, 1+, electron
D. 1, 2+, electron
E. 0, 0, proton

__________13. Which of the following processes should have $\Delta S < 0$?

A. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
B. $H_2O(s) \rightarrow H_2O(g)$
C. $2\ NO_2(g) \rightarrow N_2O_4(g)$
D. $NaCl(s) + H_2O(l) \rightarrow NaCl(aq)$
E. None of the above

__________14. During ________ only energy is released.

A. Positron emission
B. Alpha decay
C. Beta decay
D. Gamma decay
E. All of the above

__________15. Values of E° for the Ce^{4+}/Ce^{3+} and Fe^{2+}/Fe half cells are 1.72 and -0.44V, respectively. From these data you can conclude that:

A. Ce^{4+} will oxidize Fe^{2+}
B. Ce^{3+} will oxidize Fe
C. Ce^{3+} is a better oxidizing agent than Fe^{2+}
D. Ce^{4+} is a better oxidizing agent than Fe^{2+}
E. All of the above

___________16. For the reaction

$2Ag^{+} + Zn \rightarrow 2Ag + Zn^{2+}$

E°cell = 1.56 V. What is the corresponding value of $\Delta G°$?

A. - 301 kJ/mol
B. 301 kJ/mol
C. 301 J/mol
D. - 301 J/mol
E. None of the above

___________17. Energy is measured in which of the following units?

A. Newton
B. Joules
C. Pascal
D. Pound-force
E. All of the above

___________18. Which of the following statements is(are) true for all voltaic (or galvanic) cells?

(I) Reduction occurs at the cathode.
(II) The anode gains mass during discharge (note: this means operation of the cell.)
(III) The voltage is less than or equal to zero.

A. only III
B. only II
C. only I
D. II and III
E. I, II, and III

___________19. If a silver strip were immersed in an aqueous solution containing Cu^{2+} ions, what would you expect to happen?

A. Copper would be deposited on the silver strip.
B. No reaction would occur.
C. Cu^{2+} ions would be reduced.
D. Ag would be oxidized.
E. All of the above

____________20. For the reaction

$2H^{+}\ Mg \rightarrow H_2 + Mg^{2+}$

$\Delta G°$ = -457 kJ/mol. What is the value of $E°(Mg^{2+}/Mg)$?

A. - 2.37 V
B. - 4.74 V
C. + 4.74 V
D. + 2.37 V

__________21. Gold nanoparticles exhibit a variety of color characteristics at which relative scale?

A. 10^{-10}
B. 10^{-9}
C. 10^{-8}
D. 10^{-7}
E. 10^{-6}

__________22. The formation of 1/2A2 + 2B2 + C → CAB4 has an enthalpy of formation of -104 kJ and change in entropy of -60.8 J/K at 30°C. What is the free energy and spontaneity of the reaction?

A. - 85.6 kJ, spontaneous
B. + 102 kJ, not spontaneous
C. -102 kJ, spontaneous
D. + 85.6 kJ, not spontaneous
E. None of the above

__________23. Alloy of copper and zinc is known as:

A. Brass
B. Bronze
C. Duralium
D. Nichrome
E. Mutz

___________24. The process by which a body of water becomes enriched in dissolved nutrients such as phosphates that stimulate the growth of aquatic plant life usually resulting in the depletion of dissolved oxygen

A. Ozone depletion
B. Photochemical smog
C. Greenhouse effect
D. Eutrophication
E. Global warming

___________25. Which one of the following statements is TRUE?

A. Entropy increases when a liquid freezes at its melting point.
B. For a spontaneous process $\Delta G > 0$.
C. The number of microstates available to a system is a measure of its entropy.
D. Entropy of the pure crystalline solid is zero at 0°C.
E. All of the above

____________26. These polymers cannot be recycled.

A. Thermoplastics
B. Thermosets
C. Condensation polymers
D. Addition polymers
E. All of the above

____________27. What is the reduction potential for the half-reaction at 25°C

$Al^{3+} + 3e^- \rightarrow Al$, if $[Al^{3+}] = 0.10$ M and E° = -1.66 V?

A. -1.84 V
B. -1.60 V
C. -1.64 V
D -1.66 V
E. -1.72 V

____________28. A piston cylinder contains air at 600 kPa, 290 K and a volume of $0.01 m^3$. A constant pressure process give 54 kJ of work out. Find the final volume of the air.

A. $0.05 m^3$
B. $0.01 m^3$
C. $0.10 m^3$
D. $0.15 m^3$
E. None of the above

____________29. A spontaneous process

A. is reversible.
B. is irreversible.
C. maybe reversible or irreversible depending on whether equilibrium is maintained throughout the process.
D. maybe reversible or irreversible depending on the value of ΔS.
E. maybe reversible or irreversible depending on the value to T.

____________30. A drug used to treat hypertension undergoes a decomposition reaction to give an insoluble product. Calculate the temperature at which this reaction starts to become spontaneous if the enthalpy of reaction is 51 kJ/mol and the entropy of the reaction at this temperature is 118.74 J/mol-K.

A. $T > 430$ K
B. $T < 430$ K
C. $T = 430$ K
D. $T \geq 430$ K
E. $T \leq 430$ K

___________31. Brass is an alloy of

A. copper and zinc
B. tin and zinc
C. copper and tin
D. copper and aluminium
E. tin and aluminium

___________32. The work done by a closed system in a reversible process is always _____ that done in an irreversible process.

A. Less than
B. More than
C. Less than or equal to
D. More than or equal to
E. Equal to

___________33. Equal masses of two substances, A & B, each absorb 25 Joules of energy. If the temperature of A increases by 4 degrees and the temperature of B increases by 8 degrees, one can say that

A. the specific heat of A is double that of B
B. the specific heat of B is double that of A
C. the specific heat of B is negative
D. the specific heat of B is triple that of A

___________34. For a voltaic (or galvanic) cell using Ag|Ag+ (1.0 M) and Zn|Zn2+ (1.0 M) half-cells, which of the following statements is incorrect?

A. The zinc electrode is the anode.
B. Electrons will flow through the external circuit from the zinc electrode to the silver electrode.
C. Reduction occurs at the zinc electrode as the cell operates.
D. The mass of the zinc electrode will decrease as the cell operates.
E. The concentration of Ag+ will decrease as the cell operates.

___________35. What is the ΔE for a system which has the following two steps?

Step 1: The system absorbs 60 J of heat while 40 J of work are performed on it.
Step 2: The system releases 30 J of heat while doing 70 J of work.

A. 100 J
B. 90 J
C. 30 J
D. 0 J

___________36. If 25 J are required to change the temperature of 5.0 g of substance A by 2.0°C, what is the specific heat of substance A?

A. 250 J/g-°C
B. 63 J/g-°C
C. 10 J/g-°C
D. 2.5 J/g-°C

___________37. The word “polymer” meant for a material made from ________.

A. Single entity
B. Two entities
C. Multiple entities
D. Any entity
E. All of the above

___________38. Consider a process for which ΔH = 211 kJ and ΔS = -57 J/K. How will raising the temperature affect ΔG for this process?

A. ΔG will increase
B. ΔG will decrease
C. ΔG will not change
D. The effect on ΔG cannot be predicted from the information given.

___________39. The trapping of the sun's warmth in a planet's lower atmosphere due to the greater transparency of the atmosphere to visible radiation from the sun than to infrared radiation emitted from the planet's surface.

A. Ozone depletion
B. Photochemical smog
C. Greenhouse effect
D. Eutrophication
E. Global warming

___________40. Uranium-238 decays to form thorium-234. Which of the following is this an example of?

A. Positron emission
B. Alpha decay
C. Beta decay
D. Gamma decay

___________41. The reduction of the protective layer of ozone in the Stratosphere by chemical pollution. In the stratosphere, small amounts of ozone are constantly being made by the action of sunlight on oxygen.

A. Ozone depletion
B. Photochemical smog
C. Greenhouse effect
D. Eutrophication
E. Global warming

____________42. Bronze is an alloy of

A. copper and zinc
B. tin and zinc
C. copper and tin
D. copper and aluminium
E. tin and aluminium

____________43. Which of the following is true for a closed system?

A. Mass entering is the same as the mass leaving
B. Mass does not leave nor enter the system
C. Mass entering is more than the mass leaving
D. Mass entering is less than the mass leaving
E. None of the above

____________44. Which of the following statements best describes the Second Law of Thermodynamics?

A. The internal energy of the universe is constant.
B. Energy can neither be created nor destroyed.
C. When an isolated system undergoes a spontaneous change, the entropy of the system will increase.
D. At absolute zero, the entropy of a perfect crystal is considered to be zero.
E. All of the above.

____________45. Atomic packing factor is

A. Distance between two adjacent atoms
B. Projected area fraction of atoms on a plane
C. Volume fraction of atoms in a cell
D. All of the above
E. None of the above

____________46. The Third Law of Thermodynamics states:

A. If object A is in thermal equilibrium with object B, and object B is in thermal equilibrium with object C, then object A is in thermal equilibrium with object C.

B. The entropy of the universe increases for reversible processes.
C. $\Delta S = 0$ for a pure element in its most stable state at standard conditions.
D. $S = 0$ for a perfect crystal of a pure substance at 0 K.
E. All of the above

___________47. In which equation is the metal reduced?

A. $CuCO_3 + 2HCl \rightarrow CuCl_2 + CO^2 + H_2O$
B. $Mg + 2HCl \rightarrow MgCl_2 + H_2$
C. $2[MnO4]^- + 5[C_2O_4]_{2-} + 15H_+ \rightarrow 2Mn^{2+} + 10\ CO_2 + 8H_2O$
D. $[Cr_2O_7]^{2-} + 2[OH]^- \rightarrow 2[CrO_4]^{2-} + H_2O$
E. None of the above

___________48. In an open system, for a maximum work, the process must be entirely

A. Irreversible
B. Reversible
C. Constant pressure
D. Constant volume
E. None of the above

___________49. Which of the following statements is FALSE?

A. Oxidation and reduction half-reactions occur at electrodes in electrochemical cells.
B. All electrochemical reactions involve the transfer of electrons.
C. Reduction occurs at the cathode.
D. Oxidation occurs at the anode.
E. None of the above.

___________50. Noxious haze of chemical droplets and ozone, resulting from sunlight induced chemical reaction between industrial and automobile pollutants mainly nitrogen dioxide and hydrocarbons. It not only reduces visibility and irritates eyes but also affects respiratory system and causes severe damage to leafy plants.

A. Ozone depletion
B. Photochemical smog
C. Greenhouse effect
D. Eutrophication
E Global warming

LABORATORY

ACTIVITY 01: CHEMICAL LABORATORY SAFETY

Introduction

A laboratory is a place wherein teaching and learning happens to demonstrate application of chemical concepts and principles in an experimental form. It is also a place wherein a research is conducted for improvement of society. Working in a laboratory is an integral part of undergraduate chemistry courses wherein students will work on a series of experiments. Thus, the activities in the laboratory is associated with potential exposure to hazardous materials and risk of occurrence of accidents.

Chemical safety is the application of best practices in handling chemicals and working processes. It involves understanding the physical, chemical, and toxicological information of hazardous chemicals. Factors such as (1) environmental including facilities, location, equipment, protocols and standards, (2) personal including attitude, beliefs, personality, knowledge, skills, and abilities; and (3) behavioral including safe and risky processes contributes to safety. Therefore, a safety working environment is a responsibility of everyone. Chemical safety awareness is necessary to create and ensure a safety learning environment.

Personal Safety

1. Wear proper eye protection. Use protective eyewear such as laboratory goggles. Avoid using contact lenses when performing experiments.
2. Wear appropriate protective clothing and footwear. An appropriate lab gown should cover your legs to the knees. Do not wear high heal shoes, sandals, or slippers. Remove your labgown when outside the laboratory.
3. Wearing gloves will protect the hands from chemicals. There are many different types of glove depending on materials or substances which you will be working with. Remove your gloves before using an instrument and leaving the laboratory. Dispose it properly.
4. Mask will protect you from inhaling vapors and particulates. There are different types of mask depending on the materials or substances which you will be working with.
5. Long hair must be tied up. Use of hairnet is also prescribed.
6. Remove all jewelries and accessories when performing an experiment
7. Do not eat, drink, smoke, use medication or apply cosmetics in the chemical laboratory and storage.
8. Never engage in pranks and other acts of mischief. No horse playing
9. Always read the labels of all chemical reagent that you will use in the experiment. When you prepare a solution, label your sample with paper, followed by a clear tape. This will minimize the possibilities of unreadable label.
10. Put your bags on the designated areas. Avoid putting your bags in areas that will block emergency exit and electrical panels.
11. Familiarize yourself on the location of fire extinguisher, emergency exit, safety cabinet, eyewash, and laboratory shower.
12. Do not perform unauthorized experimental work, mixed chemical reagents that is not in the procedure.
13. Never work alone. Make sure somebody is aware that you are working.
14. Always wash your hands properly.
15. Dispose all the chemical waste in an appropriate waste bottle.

16. Report any accident to the instructor in charge. Broken glass and ceramics should be carefully removed, and spills should be removed based on the instructions for their removal. See emergency measures for instructions. Do not panic.

Chemical Hazard Information

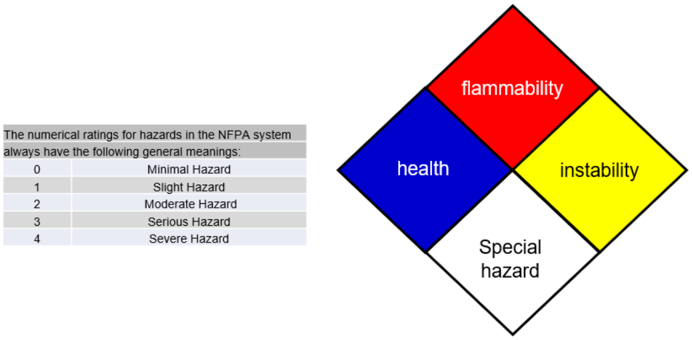
All chemicals are potentially harmful. Avoid direct contact with any chemical. Some substances now considered to be non-hazardous may, in the future, be found to cause illness. It is especially important to keep chemicals away from hands, face, and clothing, including shoes. Many substances are readily absorbed through intact skin and inhalation. Chemicals can also enter the body, through the mouth, and by contamination of the hands. Chemicals can also be transferred to the eyes from the hands.

There are several sources of information regarding the hazards presented by the chemical reagents you may encounter in a chemistry laboratory. Chemical containers are often marked with hazard labels such as the NFPA hazard diamond and the EU. hazard symbols. These labels communicate a wealth of information about the hazards posed by the chemical.

Safety Data Sheet (MSDS) is a technical document that contains information on the potential hazards and ways to handle the chemical products for safety purposes.

NFPA Diamond Chemical Hazard System

The NFPA hazard system is used to provide visual representation of the potential hazards of a certain chemical. It used color codes, numbers, and symbols for personnel to identify the hazards of a chemical that may impose during a fire.



The numerical ratings for hazards in the NFPA system always have the following general meanings:

0	Minimal Hazard
1	Slight Hazard
2	Moderate Hazard
3	Serious Hazard
4	Severe Hazard

Figure 1.1 NFPA diamond

Table No 1.1 NFPA hazard rating descriptions for health hazards, flammability hazards, and instability hazards.

Number Code	Blue	Red	Yellow
0	No unusual hazard	Not combustible	Not reactive when mixed with water
1	May be irritating	Combustible if heated	May react if heated or mixed with water but not violently

2	May be harmful if inhaled or absorbed	Combustible liquid flash point of 100 ^{0}F to 200 ^{0}F	Unstable or may react violently if mixed with water
3	Corrosive or toxic. Avoid skin contact or inhalation	Flammable liquid flash point below 100 ^{0}F	Explosive if shocked, heated under confinement or mixed with water
4	May be fatal on short exposure. Protective equipment required	Flammable gas or extremely flammable liquid	Explosive material at room temperature

Table No 1.2 NFPA special hazards symbols and meaning.

OX	Oxidizer, a chemical which can greatly increase the rate of combustion/fire.
SA	Gases which are simple asphyxiants. Used only for nitrogen,helium, neon, argon, krypton, and xenon.
W	Unusual reactivity with water. This indicates a potential hazard using water to fight a fire involving this material.

EU Chemical Hazard Symbols

A hazard pictogram symbol that can be used to classify and label hazardous chemicals in the European union.

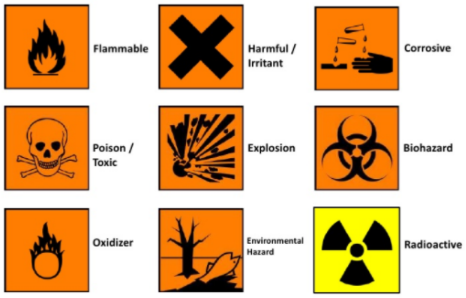


Figure 1.2 European Union hazard labels with their meaning and code.

Assessment:

1. In heating solutions using a test tube, always point a test tube ________
A. away from you and toward others
B. away from you and others
C. toward you and others
D. toward you and away from others

2. To safely smell a chemical in the lab _________
A. smell it slowly
B. inhale the fumes directly from the container
C. heat the substance before smelling
D. gently wave the fumes toward your nose using a wafting motion

3. When mixing acid and water
a. pour water into acid
b. let the teacher pour them
c. pour them at the same time
d. pour acid into water

4. The desire to maintain a safe laboratory environment for all begins with _________
a. prevention
c. microbiology
b. ubiquity
d. accidents

5. When a chemical splashes in the eye rinse for ________
a. 10 seconds c. 5 minutes b. 30 seconds d. 15 minutes

6. When working in the laboratory with chemicals, what personal protective equipment (PPE) should be worn at all time?
a. Always wear goggles and lab coats. Gloves should also be worn when needed
b. Goggles only
C. lab coats only
D. None of the above

7. The MSDS is included with all chemical shipments and describes the safety precautions and proper disposal of the chemicals. MSDS stands for ____.
A. Material Safety Disposal Stage
B. Material Safety Data Sheet
C. Master Safety Distribution Sheet
D. Master Safety Disposal Sheet

8. Which of the following colors used on the "NFPA diamond" chemical hazard warning label represents the health hazard?
A. Red
B. Blue
C. Yellow
D. White

9. The sign shown in figure 1.1 indicates what type of safety hazard?

Figure 1.1
A. Toxic – poisonous if touched, swallowed, or inhaled
B. Chemical – hazardous liquids; danger to skin and other materials
C. Biological – harmful to humans.
D. Radioactivity – radioactive materials; use caution

10. The sign shown in figure 1.2 indicates what type of safety hazard?


Figure 1.2

A. Toxic – poisonous if touched, swallowed, or inhaled
B. Chemical – hazardous liquids; danger to skin and other materials
C. Biological – harmful to humans.
D. Radioactivity – radioactive materials; use caution

11. The sign shown in figure 1.3 indicates what type of safety hazard?


Figure 1.3
A. Toxic – poisonous if touched, swallowed, or inhaled
B. Chemical – hazardous liquids; danger to skin and other materials
C. Flammable – possible burn hazard; use caution
D. Radioactivity – radioactive materials; use caution

12. The sign shown in figure 1.4 indicates what type of safety hazard?

A. Irritant - wear gloves and lab coats to protect skin.
B. Toxic – poisonous if touched, swallowed, or inhaled
C. Flammable – possible burn hazard; use caution
D. Radioactivity – radioactive materials; use caution

13. Which of the sign shown below indicates warning about corrosive chemicals?


A


B


C


D

14. Which of the following colors used on the "NFPA diamond" chemical hazard warning label represents the flammability?
A. Red

B. Blue
C. Yellow
D. White

15. Which of the sign shown below indicates warning about explosive chemicals?


A


B


C


D

16. Which of the following pair is not correct about NFPA diamond chemical label hazard warning?
A. Blue: health
B. Red: flammability
C. Red: 0 non-flammable
D. Blue: 0 highly toxic

17. Which of the following is TRUE about the symbol shown below about a certain chemical?
A. The chemical is highly flammable.
B. The chemical is highly flammable and highly flammable
C. The chemical is highly flammable, highly toxic and highly unstable
D. The chemical is highly toxic but not flammable.

18. If you injure yourself or others, _______.
a. don’t tell anyone
b. tell the teacher immediately
c. wait until the end of the experiment to tell the teacher
d. wait until after class to go to the nurse

19. Is it permissible to have any drink or food in the laboratory?
a. Yes
b. Never! There is no eating, no drinking, and no smoking permitted in the labs.
c. Water only
d. Food only

Part II. Given the following images, identify the safety equipment and write its important use/function.

A. 	B. 	C. 

ACTIVITY 02: MEASUREMENTS

The International System of Units, abbreviated as SI, is the main system of measurement units used in science. The seven base units are mole (mol), mass (kg), length (m), time (s), temperature (K), electric current (amp), and luminous intensity (candella).

Table 3.1 Prefixes used with SI Units

Prefix	**Abbreviation**	**Multiplicative Factor**	**Multiplicative Factor in Scientific Notation**
giga	G	1,000,000,000	10^9
mega	M	1,000,000	10^6
kilo	k	1,000	10^3
deca	D	10	10^1
Base (gram, meter, liter, mole)			
deci	d	1/10	10^{-1}
centi	c	1/100	10^{-2}
milli	m	1/1,000	10^{-3}
micro	µ	1/1,000,000	10^{-6}
nano	n	1/1,000,000,000	10^{-9}
pico	p	1/1,000,000,000,000	10^{-12}
femto	f	1/1,000,000,000,000,000	10^{-15}

Table 3.2 Common Conversions Between Metric and English Systems

1 m = 39.36 in = 3.28 ft = 1.09 yd
I in = 2.54 cm
1kg = 2.20 lb
1 lb = 454 g
1L = 1.06 qt
1 L = 0.26 gal
1 oz = 26.57 mL

Temperature - a property of matter which represents a quantitative measurement of the average kinetic energy of the substance. The following are the conversion of temperature scale

$^{0}C = 5/9 \times (^{0}F - 32)$
$^{0}F = (9/5 \times {}^{0}C) + 32$
$K = {}^{0}C + 273.15$

Sample Problem 3.1 Convert 172.9 ^{0}F to degrees Celsius

$^{0}C = 5/9 \times (^{0}F - 32)$
$^{0}C = 5/9 \times (172.9 - 32) =$ **78.3 ^{0}C**

Density - mass of an object divided by its volume; it describes the amount of matter contained in a given amount of space.

$$\boldsymbol{\rho = \frac{mass\ (g)}{volume\ (mL)}}$$

Specific gravity - ratio of density of the substance and density of water at the same temperature.

$$\boldsymbol{sp\ gr = \frac{\rho_{substance}}{\rho_{water}}}$$

Sample Problem 3.2 Density Determination A piece of platinum metal with a density of 21.5 g/mL has a volume of 4.49 mL. What is its mass?	
Given	ρ = 21.5 g/mL, V = 4.49 mL
Ask for	mass (g)
Strategy	Rearrange the equation below and substitute the values $\boldsymbol{\rho = \frac{mass\ (g)}{volume\ (mL)}}$ $mass = \rho\ x\ V = 21.5 \frac{g}{mL} x\ 4.49\ mL = 96.535 = \mathbf{96.5}$

II. Making Measurement in the Lab

A. Significant Figures - refers to the number of important single digits which is meaningful in measurement.

Table 3.3 Rules in Significant Figure

Rule	**Example**	**Answer**
1. Any digit that is not zero is significant	1.234 kg	4 SF
2. Zeros between nonzero digits are significant	606 m	3 SF
3. Zeros to the left of the first nonzero digit are not significant	0.08 L	1 SF
4. If a number is greater than 1, then all zeros to the right of the decimal point are significant	2.0 mg	2 SF
5. If a number is less than 1, then only the zeros that are at the end and in the middle of the number are significant	0.00420 g	3 SF

Significant Figures in Unit Operation

Addition and Subtraction

When adding or subtracting the set of data with varied number of significant figures, the data which the **least number of decimal places** will determine the number of the sum or difference of the data.

Example:

$$\begin{array}{rl} 89.332 & \\ +\ 1.1 & \longleftarrow \text{1 decimal place} \\ \hline 90.432 & \longleftarrow \mathbf{90.4} \end{array} \qquad \begin{array}{rl} 3.70 & \longleftarrow \text{2 decimal places} \\ -\ 2.913 & \\ \hline 0.787 & \longleftarrow \mathbf{0.79} \end{array}$$

Multiplication and Division

For the product or quotient of the data with varied number of significant figures the data with the least number of significant figures determines them.

Example:

$$\underset{\underset{\text{3 significant figures}}{\uparrow}}{4.51} \times 3.6666 = 16.536366 = \underset{\underset{\text{round off to 3 significant figures}}{\uparrow}}{\mathbf{16.5}}$$

$$\underset{\underset{\text{2 significant figures}}{\uparrow}}{6.8} \div 112.04 = 0.0606926 = \underset{\underset{\text{round off to 2 significant figures}}{\uparrow}}{\mathbf{0.061}}$$

Exact Numbers

Numbers from definitions or numbers of objects are considered to have an infinite number of significant figures

The average of three measured lengths; 6.64, 6.68 and 6.70?

$$\frac{6.64 + 6.68 + 6.70}{3} = 6.67333 = 6.67\cancel{7}$$

Practice Problem	**Answer**
1. How many significant figures are in each of the following measurements?	
2. The speed of sound in air is about 343 m/s. What is this speed in miles per hour?	
3. Gold is a precious metal that is chemically unreactive. It is used mainly in jewelry, dentistry, and electronic devices. A piece of gold ingot with a mass of 301 g has a volume of 15.6m L. Calculate the density of gold.	
4. Solder is an alloy made of tin and lead that is used in electronic circuits. A certain solder has a melting point of 224°C.	

Assessment

Part I. Multiple Choice. Write the capital letter of your choice on the answer sheet. Please refer to the instruction on page X.

1. All of the following are SI base units except:

A. meter C. Kelvin
B. gram D. second

2. The prefix "milli" and the prefix "micro" correspond, respectively, to the factors:
A. 10^{-3} and 10^{-12} C. 10^{-1} and 10^{-6}.
B. 10^{-6} and 10^{-9} D. 10^{-3} and 10^{-6}.

3. Which of the following is longest?
A. 3.0×10^{-4} m C. 3.0 nm
B. 300 pm D. 3.0×10^{-10} cm

4. Without doing a calculation explain which of the following represents a higher temperature?
A. 0 K C. 0 °C
B. 270 K D. 0 °F

5. Which of the following occupies the most volume?
A. 1.36 kilograms of mercury (density = 13.6 g/mL)
B. 4.50 pounds of gold (density = 19.3 g/mL)
C. 5.07 fluid ounces of water (32 fl oz = 1 qt)
D. 200 milliliters of methanol

6. How many significant figures should the answer to the following calculation have?

$$(1.4312 - 1.1 \times 10^{-2}) \div (1.0712 \times 10^{-4})$$

A. 2 C. 5
B. 3 D. 4

7. Ethylene glycol has a density of 1.11 g/mL. What is the volume occupied by 30.0 g of ethylene glycol?
A. 27.0 mL C. 33.3 mL
B. 31.1 mL D. 30.0 mL

Part II. Problem Solving. Solve the following problems. Show your complete solution.

1. Calculate the length of a steel cable (density 7.91 g/cm^3) with a mass of 160.0 g and cross-section area of 0.500 cm^2.
2. A weatherman incorrectly stated that the temperature was 85°F, 35°C. If the Fahrenheit temperature was correct, how far off was the Celsius temperature?

EXPERIMENT 1: Heat of Combustion

Introduction:

The heat of combustion is the liberated energy that occurs when a substance undergoes complete combustion, usually in an oxy gen – rich environment, at constant pressure. This value is used to quantify the performance of a fuel in combustion systems (e.g. motors, engines in cars, turbines). Fuels are materials that are used to release energy (work or heat) via a chemical reaction. These makes fuels a very crucial group of substances especially in the modern civilization. Common fuels include gasoline, petroleum, and diesel. These fuels are commonly composed of hydrocarbons of differing molecular weights and other organic compounds. Combustion of these hydrocarbons gives off carbon dioxide and water as its major products, with a release of large amounts of heat.

In this experiment, the heat of combustion of common fuels (which are not normally seen as fuels per se) would be studied, using a simple calorimeter model.

Objectives:

1) Determine heats of combustion of a 70% isopropyl alcohol.

Personal Protective Equipment:

Laboratory gown, heat resistant gloves, eye protection

Methodology

1) Measure 100 mL of water and pour it inside a clean, dry aluminum can. Record the initial temperature of the water.
2) Fill the fuel lamp with 70% isopropyl alcohol. Record the volume of the fuel.
3) Settle the aluminum can on top of the tripod, while the fuel lamp in the bottom. Ignite the lamp, making sure the fire reaches the aluminum can.
4) Stir the water gently with the thermometer and watch the temperature. When the temperature has increased by 20 °C, put off the flame of the lamp.
5) Record the mass final volume of the fuel.
6) Repeat the experiment at least twice for the same fuel, making sure that fresh water is used inside the can.
7) After at least three trials, use another fuel.
8) Compute for the energy transferred to the water by the equation

$$q=m_{H_2O}Cp\Delta T$$

Assume that the density of water is 1.00 g /mL, and the specific heat is 4.18 J / g·°C. The relative density (water =1) of 70% isopropyl alcohol is 0.79.

Assessment:

1) For each replicate experiment, perform the following calculations:
    a. The mass of the fuel burnt, m_{fuel}
    b. The amount of moles of the fuel burnt, n_{fuel}
    c. The molar enthalpy of combustion of the fuel by the equation

$$\Delta_C H = \left(\frac{q}{n_{fuel}}\right)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

2) Would there be a change in the value of the enthalpy of combustion if the water is heated until a 30 °C change is observed, rather than 20 °C? Why or why not?

EXPERIMENT 2: Calorimetry

Introduction:

Calorimetry is a method of measuring the heat transfer within a chemical reaction or other physical processes, such as a change between different states of matter, or dissolving of a substance in a liquid. Its name is derived from the Greek words that mean heat and measurement.

Heat is a form of energy, and such it abides to the law of conservation of energy. The realization of this concept would then initiate the studies of the branch of chemistry that is thermodynamics. Calorimetry is also the only experimental method allowing for direct measurements of various physical and chemical processes and reactions, such as the specific heat, and various types of molar enthalpies of different processes.

In this experiment, calorimetric measurements would be conducted for heat of neutralization, heat of dissolution and specific heat, using a simple calorimeter model called the “coffee cup calorimeter”.

Objectives:

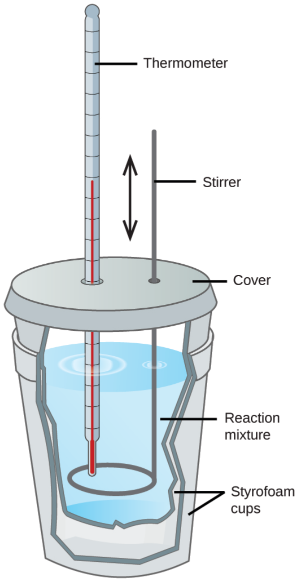
1) Determine the calorimeter constant of a coffee cup calorimeter.
2) Determine the enthalpy of dissolution of the table salt.

Personal Protective Equipment:

Laboratory gown, heat resistant gloves, eye protection

Methodology:

Setup A Calorimeter Constant



1) Setup a coffee cup calorimeter by obtaining two Styrofoam cups nestled at each other.
2) Place the cups in a 400 mL beaker to elevate the calorimeter off the top of the table.
3) Obtain the cover for the cup and create two holes in which the stirrer and the thermometer would fit snuggly. It should look like the figure below.
4) Obtain 50.0 mL of water and pour it in the calorimeter. Measure another 50.0 mL of water and pour into a dry 250 mL beaker.
5) Stir the calorimeter contents for at least five minutes and then record the temperature inside the calorimeter. Designate this as T_C.
6) Meanwhile, heat the water in the beaker and stir using a different thermometer until it reaches a temperature of 70 – 80 °C.
7) Remove the beaker from heat, record the temperature as T_H, and open the calorimeter to pour the hot water inside and replace the top. This part should be done as swiftly as possible.

8) Stir the contents of the calorimeter while recording the temperature at 15 second intervals. Record the highest temperature obtained in 3 – 5 minutes as T_F.
9) Compute for the calorimeter constant C by use of the following formula:

$$C=\left[\frac{(50.0\text{ g})(T_H - T_F) - (50.0\text{ g})\ (T_F - T_C)}{(T_F - T_C)}\right]\left(4.184\frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}}\right)$$

10) Repeat steps 4 – 9 for a second determination of C. Swap the thermometers in this second trial.

Setup B Enthalpy of Dissolution

1) Dry the calorimeter setup and reassemble it.
2) Weigh out approximately 2 grams of table salt and record the exact amount in grams.
3) Measure 50.0 mL of water and pour it in the calorimeter. Stir the calorimeter and record the temperature inside as T_I.
4) Open the calorimeter, add the salt and close it.
5) Stir the solution and record the temperature in 15 second intervals. Record the highest temperature obtained in 3 – 5 minutes as T_F.
6) Use these temperatures and the value of C from Setup 1 to determine the enthalpy of dissolution using the following formula:

$$q=\left[(52\text{ g})\left(4.184\frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}}\right)+C\right](T_F - T_I)$$

$$\Delta_{\text{dis}}H=\left(\frac{q}{0.100\text{ mol}}\right)\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)$$

Assessment:

Setup A

First Trial	**Second Trial**
T_C =	T_C =
T_H =	T_H =
T_F =	T_F =
C =	**C =**

Include your computations

Setup B

Table Salt (NaCl)
T_I = **T_F =** **q =** **$\Delta_{dis}H$ =**

Include your computations

1) What errors would have happened if you used a calorimeter that has not been dried?
2) Let's say that an inventor creates a new instrument to control temperature using the salts given in the experiment. Which of these would be practical to use in a tropical climate, and which would be practical in an arctic environment? Why did you say so?

ACTIVITY 03: Nuclear Reactions, Binding Energy and Rate of Decay

Part I: Nuclear Reactions

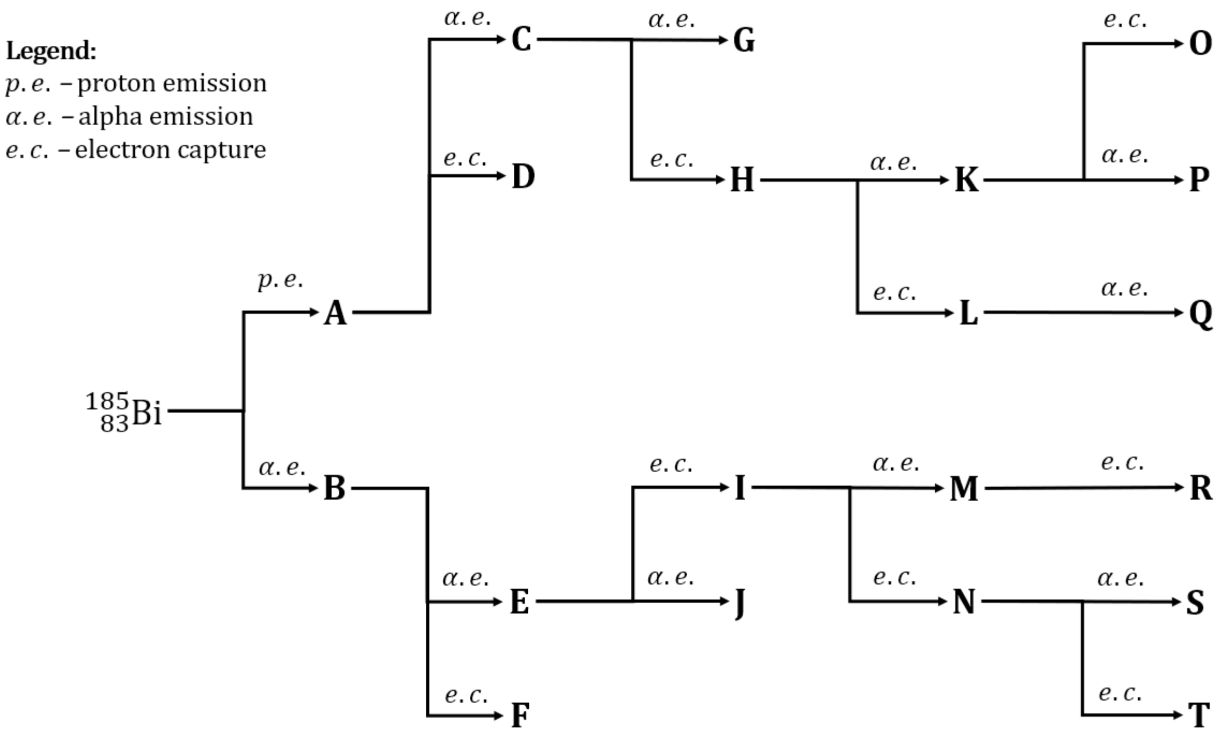
Write your answers to the following under the header <u>Part I</u>:

1. Identify the possible types of nuclear decay based on the given parent nuclide and daughter nuclide. Write also the balanced nuclear reaction based on your choice of nuclear decay.

    a. Hafnium – 174 to Ytterbium – 170
    b. Rhenium – 188 to Osmium – 188
    c. Gold – 193 to Platinum – 193
    d. Bismuth – 185 to Lead – 184
    e. Fluorine – 17 to Oxygen – 17
    f. Fluorine – 16 to Oxygen – 15
    g. Fluorine – 20 to Neon – 20
    h. Boron – 16 to Boron – 15
    i. Astatine – 213 to Bismuth – 209
    j. Lawrencium – 258 to Mendelevium – 254

2. From the given parent nuclides and the type of nuclear decay, write the balanced nuclear reactions for each of the given.
    a. Oxygen – 19 undergoes beta emission
    b. Neon – 19 undergoes positron emission
    c. Beryllium – 8 undergoes alpha emission
    d. Sodium – 22 undergoes electron capture
    e. Lithium – 10 undergoes neutron emission
    f. Lanthanum – 128 undergoes electron capture
    g. Xenon – 122 undergoes positron emission
    h. Antimony – 130 undergoes beta emission
    i. Neodymium – 144 undergoes alpha emission
    j. Europium – 130 undergoes proton emission

3. Identify the nuclides that if the letters are replaced by them, the reaction would be correct. Write your answer before the letter that it should replace.



Part II: Binding Energy

Write your answers to the following under the header Part II. Show your complete solutions.

1. Calculate the value for the mass defect of an atom of the following:
    a. Helium – 4 (isotopic mass = 4.002602 u)
    b. Lithium – 7 (isotopic mass = 7.016004 u)
    c. Beryllium – 9 (isotopic mass = 9.012182 u)
2. Calculate the value for the mass defect of a mole of the following:
    a. Boron – 15 (isotopic mass = 15.031088 u)
    b. Carbon – 14 (isotopic mass = 14.003241 u)
    c. Nitrogen – 17 (isotopic mass = 17.008449 u)

3. Fermium – 246 could either undergo an alpha decay, a positron emission or a spontaneous fission yielding Uranium – 235 and Oxygen – 16. What would be the energy released by one mole of Fermium – 246 as it undergoes each of the given nuclear reactions?

Isotope	Atomic Mass (u)
${}^{246}_{100}\mathrm{Fm}$	246.075350
${}^{242}_{98}\mathrm{Cf}$	242.06370
${}^{246}_{99}\mathrm{Es}$	246.07290
${}^{235}_{92}\mathrm{U}$	235.0439299
${}^{4}_{2}\mathrm{He}$	4.001506
${}^{16}_{8}\mathrm{O}$	15.9949146

Part III: Rate of Decay

Write your answers to the following under the header Part III. Show your complete solutions.

1. Platinum has a naturally occurring radioisotope, Platinum – 190, with a half – life of 6.50 × 10^{11} years. It also has several synthetic radioisotopes with varying half – lives. For example, Platinum – 193 has a half – life of 50 years, Platinum – 188 has a half – life of 10.2 days, Platinum – 200 has a half – life of 12.5 hours, and Platinum – 179 has a half – life of 21.2 seconds.
    a. What are the decay constants of the given platinum isotopes?
    b. If hypothetically we can have 10.00 g of each isotope at the same time, what would be the remaining amount of each of the isotopes after a year?
    c. If hypothetically we can have 10.00 g of each isotope at the same time, how long will it take until the isotope samples have 1.00 g remaining?

2. The Windscale fire is an accident that happened in October 1957 in the U.K. and has a level 5 severity from the INES scale. The accident released radioactive fallout from iodine – 131, polonium – 210, and possibly strontium – 90. What amount of each of the given radioisotopes would have registered a radioactivity of 25,000 Ci?

Isotope	Atomic Mass (u)	Half – Life
${}^{131}_{53}\mathrm{I}$	130.9061246	8.02070 days
${}^{210}_{84}\mathrm{Po}$	209.9828737	138.376 days
${}^{90}_{38}\mathrm{Sr}$	89.907738	28.90 years

EXPERIMENT 3: Electrolytic Cells and Battery

Introduction:

In electrochemistry, a cell is a device that will either generate an electric current through a spontaneous chemical reaction (voltaic cell), or will facilitate such a reaction through application of electrical energy (electrolytic cell). A combination of one or more cells with some sort of external connections would then create a battery. When two different metals are connected by an electrolyte, a chemical reaction occurs at each metal surface, called electrodes, that either releases or uses electrons. When these electrodes are connected by a wire, electrons will move from one surface to the other, creating an electric current.

Batteries are great portable sources of electric energy, such as its uses in remote controls, cars, flashlights and smartphones. This portability aspect makes the batteries a very useful device for such a purpose. Some batteries could be disposed and replaced when they have no stored electrical energy left (primary batteries), or be recharged by applying an electric current (secondary batteries).

In this experiment, simple voltaic cells and batteries would be made from everyday materials.

Objectives:

1) Create coin battery.
2) Determine the required number of makeshift cells to power up various LED lights.

Personal Protective Equipment

Laboratory gown, gloves, eye protection

Methodology

1) Obtain 100 mL of water and add salt on it until no more salt dissolves (saturated solution). Add 5.0 mL of vinegar into the solution.
2) Cut the board into ½ inch squares. Soak the squares in the solution until they are thoroughly wet.
3) Remove the squares from the solution and place them in a paper towel so that the excess solution is removed. Do not dry the squares. Leave them damp.
4) Use the sandpaper to remove the copper coating from one side of at least 19 of the ten centavo coins. Leave one of the ten centavos intact. Continue the sanding until a silver color is intact in the entire side. Do not sand both sides. One side should still be having the copper coating.
5) Take one of the sanded coins with the steel side facing up (copper side down), and place one of the damp squares above it. Stack another sanded coin above, and place another of the damp squares. Continue stacking this way, making sure that the coin on top is the unsanded one. Make sure there are no touching coins, or touching squares in the stack.
6) Test the makeshift battery by connecting a red LED on each of the ends. Determine the minimum number of coins used to light the red LED. Repeat the testing using the other LEDs with different colors.

Assessment:

Number of Coins Required to Light LED

LED Color	No. of Coins
Red	
Yellow	
Green	
Blue	

1) Which LED color required the highest number of coins to light up? Which LED color required the lowest number?

2) The 10 – centavo coin, along with the 1 – centavo and the 5 – centavo in the BSP Coin Series 1995 - 2017, are copper plated steel coins, while the 25 – centavo coin is brass plated, and the 1 – peso coin in the series is nickel – plated, similar to all the BSP Coin Series 2018. Based on this information, which of the following types of coin would require the fewest number to light up a LED in the experiment: the 10 – centavo coin, the 25 – centavo coin, or the 1 – peso coin? Why do you think so?

EXPERIMENT 4: Corrosion

Introduction:

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a material (usually a metal) that results from a chemical or electrochemical reaction with its environment. In simple terms, corrosion is the natural deterioration that results when a surface reacts with its environment. Different surfaces, environments and other factors add complexity to the equation.

Like other natural hazards such as earthquakes or severe weather disturbances, corrosion can cause dangerous and expensive damage to everything from vehicles, home appliances, and water and wastewater systems to pipelines, bridges, and public buildings. Unlike weather-related disasters, however, there are time-proven methods to prevent and control corrosion that can reduce or eliminate its impact on public safety, the economy, and the environment.
In this experiment, the corrosion process is observed, as well as some causes of corrosion. Some prevention steps are also exhibited so as to display possible inhibitors of corrosion.

Objective:

1) Describe possible causes of rusting and its prevention in various conditions.

Personal Protective Equipment

Laboratory gown, gloves, eye protection

Methodology:

1) Prepare a solution using 75 mL of vinegar and 5 grams of salt. Mix thoroughly. Partly fill-in two separate containers with ¼ of this solution and add a 10 – centavo coin. Label the containers A and B.
2) After 30 minutes, remove the coins from the solution. Rinse the coin from container A and let it dry in a paper towel. The coin from container B should not be rinsed; it should be placed directly in a paper towel to dry.

Assessment:

1) Write down the observations from the performed experiment. Are there any differences and changes. Compare them to an ordinary 10 – centavo coin.
2) What are the essential components so that rusting would occur? What components speed up rusting? What components slow down or stop rusting?
3) Iron forms rust (red brown layer of oxidized iron), while copper forms patina (a green layer of oxidized copper). Although both are results of oxidation, why is patina seen as a beneficial result while rust is a hazardous occurrence?

EXPERIMENT 5: Polymers

Introduction:

One of the most widely utilized groups of materials on earth is the so called polymers. They range in application from adhesives to containers, from textiles to paints, and from gels to bullet – proof materials. With a wide array of uses, it goes to show how versatile and useful these materials are, although they are also leading causes of pollution in the environment.

Polymers are substances that are created by linking many small molecules, which are called monomers, via chemical reactions. Depending on the reaction, these may give the materials toughness, elasticity and other peculiar properties.

In this experiment, investigations on the synthesis of simple polymers from common materials and effects of different variables would be studied. It also would provide appreciation on the effects of polymers in the environment and recent studies regarding biodegradable polymers.

Objectives:

1) Synthesize an adhesive from milk and investigate the effects of varying parameters to the adhesive properties.
2) Describe the properties of common hydrogels found in hair gel and disposable diapers

Personal Protective Equipment

Laboratory gown, gloves, eye protection

Methodology

Setup A Production of Glue from Milk

1) Measure 100 mL of milk and 20 mL of vinegar into a glass container. Heat it in a hot plate or a burner. Stir constantly until small lumps start to form. Stop heating, but keep stirring until no more lumps form.
2) Let the lumps settle, then decant the liquid from the top. Filter the rest of the mixture and keep the solid part (which is called the curds.) Wash the container with water.
3) Gently squeeze off any excess liquid from the curds and then put them into the container. Add 15 mL of water and stir until the mixture is smooth.
4) Add about half a spatula of the sodium bicarbonate (baking soda) until the mixture is neutral. You can check the pH of the mixture using a litmus paper.
5) Use the glue to stick together two popsicle sticks. Only have 2 cm of the sticks overlapping and stuck together.
6) Arrange two tables or chairs about 10 cm apart. Lay your glued popsicle sticks so that they form a bridge between the two.
7) Hang a weight hanger onto the lower of the two popsicle sticks as close to the glued joint as you can. Add coins of the same kind at a time and record the force required to break the glue.

Setup B Hydrogels

Part 1

1) Put a blob of hair gel onto the Petri dish lid. A large teaspoonful is fine.
2) Gently sprinkle salt from a spatula over the hair gel.
3) Observe and describe what happens after adding salt to the hair gel.

Part 2

1) Cut the middle section out of the diaper – the thicker piece that is designed to absorb the urine. Discard the other piece.
2) Make sure the ice cream container is completely dry – wipe it with a paper towel if necessary. Any moisture in the tub stops the experiment from working properly.
3) Wear eye protection for the next step. Put the center piece of the nappy into the ice cream container and gently take it apart. Small white grains should start coming away and this is what you are trying to collect. Keep gently pulling the diaper apart until you have collected as many of the grains as you can. Do not do this roughly or you will lose your product and put a lot of dust and fluff into the air. Avoid breathing in any of the dust.
4) Remove and dispose of all the fluff and other parts of the diaper, keeping the grains in the bottom of the tub. They are heavier and fall to the bottom, which makes it easier to separate them out.
5) Estimate the volume of the grains.
6) Pour them into the large beaker and add about 100 mL of distilled water. Stir. Keep adding distilled water until no more can be absorbed and stir between each addition. Estimate the final volume of the hydrogel.
7) Add a spoonful of salt and stir.
8) Record all observations.

Assessment:

1. What do you think is the purpose of the vinegar in the first experiment?
2. Why is a bases added in the first experiment?
3. Why do hydrogels attract and retain water?
4. What effect does adding salt in a hydrogel produce?

ACTIVITY 04: Computations in Simple Atomic Crystal Structures

1. Explain how the intensive properties of a material are reflected in the unit cell. Are all the properties of a bulk material the same as those of its unit cell? Explain your answer.

2. The experimentally measured density of a bulk material is slightly higher than expected based on the structure of the pure material. Propose two explanations for this observation.

3. What is meant by the term coordination number in the structure of a solid? How does the coordination number depend on the structure of the metal?

4. Arrange the three types of cubic unit cells in order of increasing packing efficiency. What is the difference in packing efficiency between the hcp structure and the ccp structure?

5. The structures of many metals depend on pressure and temperature. Which structure—bcc or hcp—would be more likely in a given metal at very high pressures? Explain your reasoning.

6. Metallic rhodium has an fcc unit cell. How many atoms of rhodium does each unit cell contain?

7. Chromium has a structure with two atoms per unit cell. Is the structure of this metal simple cubic, bcc, fcc, or hcp?

8. The density of nickel is 8.908 g/cm3. If the metallic radius of nickel is 125 pm, what is the structure of metallic nickel?

9. An element has a density of 10.25 g/cm3 and a metallic radius of 136.3 pm. The metal crystallizes in a bcc lattice. Identify the element.

10. A 21.64 g sample of a nonreactive metal is placed in a flask containing 12.00 mL of water; the final volume is 13.81 mL. If the length of the edge of the unit cell is 387 pm and the metallic radius is 137 pm, determine the packing arrangement and identify the element.

11. Lithium crystallizes in a bcc structure with an edge length of 3.509 Å. Calculate its density. What is the approximate metallic radius of lithium in picometers?

12. A simple cubic cell contains one metal atom with a metallic radius of 100 pm:

a. Determine the volume of the atom(s) contained in one unit cell
[the volume of a sphere = $(4/3)\pi r^3$].
b. What is the length of one edge of the unit cell?
c. Calculate the volume of the unit cell.
d. Determine the packing efficiency for this structure.
e. Use the steps in Problem 11 to calculate the packing efficiency for a bcc unit cell with a metallic radius of 1.00 Å.

EXPERIMENT 6: Air Quality Monitoring

Introduction

Humans can survive for couple of days without water but the same case cannot be observed without the air we breathe. A lot of air pollutants are present in the atmosphere most of them are odorless and seems not be present.

In this experiment we are to conduct a simple experiment that will qualitatively determine the presence and amount of particulate matters in the surrounding area.

Objective

To determine the amount of air particles in nearby area.

Personal Protective Equipment

Laboratory gown, gloves, eye protection

Methodology

1) Cut a cardboard into 10 3x3 inch squares.
2) Punch a hole on an edge of a square and tie pieces of strings in the holes.
3) Smear a thin layer of Vaseline on the square.
4) Hang them in different places where you have decided to examine for air quality.
5) Wait for a week before you collect your squares.
6) Examine the results with a magnifying glass.

Assessment

1) Does the amount of particles that were collected differ from one square to another?
2) What are the possible factors that may have affected the varied amount of particles that were collected?
3) What are the possible effects from breathing highly polluted air?
4) Cite three measures that you can do to help in making the air clean.

CHEMISTRY FOR ENGINEERS - LABORATORY
SUMMATIVE EXAMINATION

INSTRUCTIONS:

1. Read the questions carefully.
2. Write the corresponding CAPITAL letter of your answer on your assessment sheet
3. Answers should all be in BLUE or BLACK ink only. Answers written in pencil will not be corrected.
4. Answers with erasures will not be corrected.

1) What does this symbol stands for?

A. Flammable
B. Explosive
C. Toxic
D. Oxidizing
E. Corrosive

2) Calculate for the percentage error for the specific heat of copper metal with an experimental value of 0.4092 J/g°C against a true value of 0.3768J/g-°C.

A. 7.92%
B. 7.33%
C. 8.60%
D. 92.08%
E. None of the above

3) What does this symbol stands for?

A. Toxic
B. Explosive
C. Flammable
D. Oxidizing
E. Corrosive

4) What does this symbol stands for?

A. Flammable
B. Explosive
C. Toxic
D. Oxidizing
E. Corrosive

5) The change of a laboratory procedure into a safer means is an example of what kind of control?

A. usage of personal protective equipment
B. administrative control
C. engineering control

D. substitution
E. elimination

6) Which of the following statements are true about hydrogels.

A. Hydrogels are polymeric compounds that are made up of carboxylic acids that ionize when submerged in water.
B. Hydrogels are polymeric compounds that has several negative charges that repels each other causing the polymer to expand.
C. Hydrogels are polymeric compounds with negative charges on which the polar water molecules are attracted which increases its viscosity.
D. A and B only
E. All of the above

7) It is a method of measuring the heat transfer within a chemical reaction or other physical processes.

A. Colorimetry
B. Calorimetry
C. Heat of Combustion
D. Calomiter
E. Heating

8) Defined as any source of potential damage, harm of adverse effects on something or someone.

A. Risk
B. Accident
C. Incident
D. Hazard
E. Safety

9) The following statements were derived from the experiment on the Production of Glue from Milk. Which of them is INCORRECT?

A. Full fat milk tends to be the strongest among the glues produced.
B. Casein is the protein molecule that formed the glue.
C. The fat in the milk prevents the casein from sticking together as effectively.
D. The glue that was produced consists particles of the protein casein that are precipitated from the milk by adding vinegar.
E. Skimmed milk tends to be the strongest among the glues produced.

10) . What does GHS stands for?

A. Globally Harmonized System
B. Global Hazard Control System
C. Globally Harmonized System of Chemical Labelling
D. Globally Harmonized System of Classification and Labelling of Chemicals
E. All are applicable

11) . The following are good laboratory practices EXCEPT:

A. When a mixture of acid to water is to be made, the acid should be added to the water
B. When a mixture of acid to water is to be made, the water should be added to the acid
C. Toxic and hazardous wastes should not be disposed in regular solid waste bins
D. All laboratory incidents should be reported to the faculty-in-charged
E. Use of proper and appropriate personal protective equipment

12) . In the Hair Gel Collapse Experiment, the trapped water was released from the polymer chain network by addition of salt to the gel. This observation is true because:

A. Ions present in the salt displaced the water molecules within the gel
B. Ions present in the salt are more strongly attracted to the polymer than water.
C. Ions present in the salt are less attracted to the polymer than water.
D. C only
E. Both A and B

13) . The method of calorimetry follows which fundamental law?

A. The Law of Definite Proportions
B. The Law of Conservation of Mass
C. The Second Law of Thermodynamics
D. The Law of Conservation of Energy
E. The Third Law of Thermodynamics

14) . A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat of the lead pellet? Specific heat of water is 4.184 J/g-°C. Density of water is 1.00 g/mL.

A. 280.33 J/g-°C
B. - 0.158 J/g°-C
C. 8.51 J/g°-C
D. 7.47 J/g-°C
E. 0.158 J/g-°C

15) . What does this symbol stands for?
A. Flammable
B. Explosive
C. Toxic
D. Oxidizing
E. Corrosive

16) . What is the polymer found in diapers that absorb water?

A. polyvinyl chloride
B. polyacetate
C. sodium polyacrylate
D. polycarbonate
E. Dacron

17) . A student conducted an experiment on calorimetry using a bomb calorimeter. 50.0 mL of water was poured into the calorimeter where the temperature was determined as 27°C. Then to it, a 50.0 mL of hot water with a temperature of 98°C was added. The final temperature of the hot and cold water mixture was determined as 56°C. What is the calorimeter constant that the student will likely to obtain? Assume the density of water is constant at 1g/mL during the whole experiment. Specific heat of water is 4.184 J/g-C.

A. 98.73 J/g-°C
B. 93.78 J/g-°C
C. 47.62 J/g-°C
D. 90.56 J/g-°C
E. 63.78 J/g-°C

18) . What does MSDS stands for?

A. Method Safety Data Sheet
B. Method Specification Data Sheet
C. Material Specification Data Sheet
D. Material Safety Data Sheet
E. None of the above

19) . In the NPFA Diamond, what does the color RED stands for?

A. Reactivity
B. Fire hazard
C. Health hazard
D. Toxicity level
E. Acidity

20) Chromium has a structure with two atoms per unit cell. What is its structure?

A. Simple cubic
B. BCC
C. FCC
D. HCP
E. None of the above

REFERENCES

Beran, J.A. **(2009)** *Laboratory Manual for Principles of General Chemistry,* 8th edition John Wiley and Sons Inc.

Brown, Lawrence and Holme, Thomas, (2011) *Chemistry for Engineering Students*, 2nd Edition, Brooks/Cole Cengage Learning, USA

Brown, T.L., Lemay Jr., H.E., Bursten, B.E., Murphy, C.J., and Woodward, P.M. (2012) *Chemistry: The Central Science*, 12th Ed., USA: Pearson Education, Inc.

Burg, D.L. (2013) *Laboratory Manual For General Chemistry*. Dephlogisticated Columbus, Ohio

Callister Jr., W., (2007) *Material Science and Engineering: An Introduction*, John Wiley & Sons, USA

Chang, Raymond (2010), *Chemistry*, 10th Edition, McGraw-Hill Companies, Inc., USA

Chang, R. and Goldsby, K. **(2019).** *Chemistry*. 13th international ed. New York: McGraw Hill Education

Ibanez, J.G., Hernandez-Esparza, M., Doria-Soriano, C., Fregoso-Infante, A., Singh,M.M. (2007) *Environmental Chemistry Fundamentals*, Springer Science+Business Media, LLC, New York, USA

Masteron, W.L., and Hurley, C.N. (2008) *Chemistry: Principles and Reactions*, 6th edition. Canada: Brooks/Cole-Cengage Learning

Polytechnic University of the Philippines – College of Science Safety Guidelines and Regulations

Roussack, O.V., Gesser. H.D., (2013). *Applied Chemistry: A Textbook of Engineers and Technologists*, 2nd Ed., London, Springer

Smith, J.M., Van Ness, H.C., Abbot, M.M. (1996) *Introduction to Chemical Engineering Thermodynamics*, 5th Ed., McGraw Hill International Editions, Chemical Engineering Series, Singapore

Spielberg, M.S. (c2007) *Principles of General Chemistry*, 2nd Edition, New York, USA.

Synder, Carl H., (2003), *The Extraordinary Chemistry of Ordinary Things*, 4th Edition, John Wiley & Sons, Inc, USA

Tordillo, J. (2019) *Simplified Engineering Thermodynamics For Thermodynamics 1 and* 2, Tordillo Publising, Cebu City, Philippines

Weiner, S.A and Harrison, B. **(2010)** *Introduction to Chemical Principles: A Laboratory Approach* Brooks Cole Cengage Learning

Whitten, K.W., Davis, R.E., Peck, M.L. and Stanley G.G (2010) Chemistry 9th Edition. USA, Brooks/Cole-Cengage Learning

APPENDICES

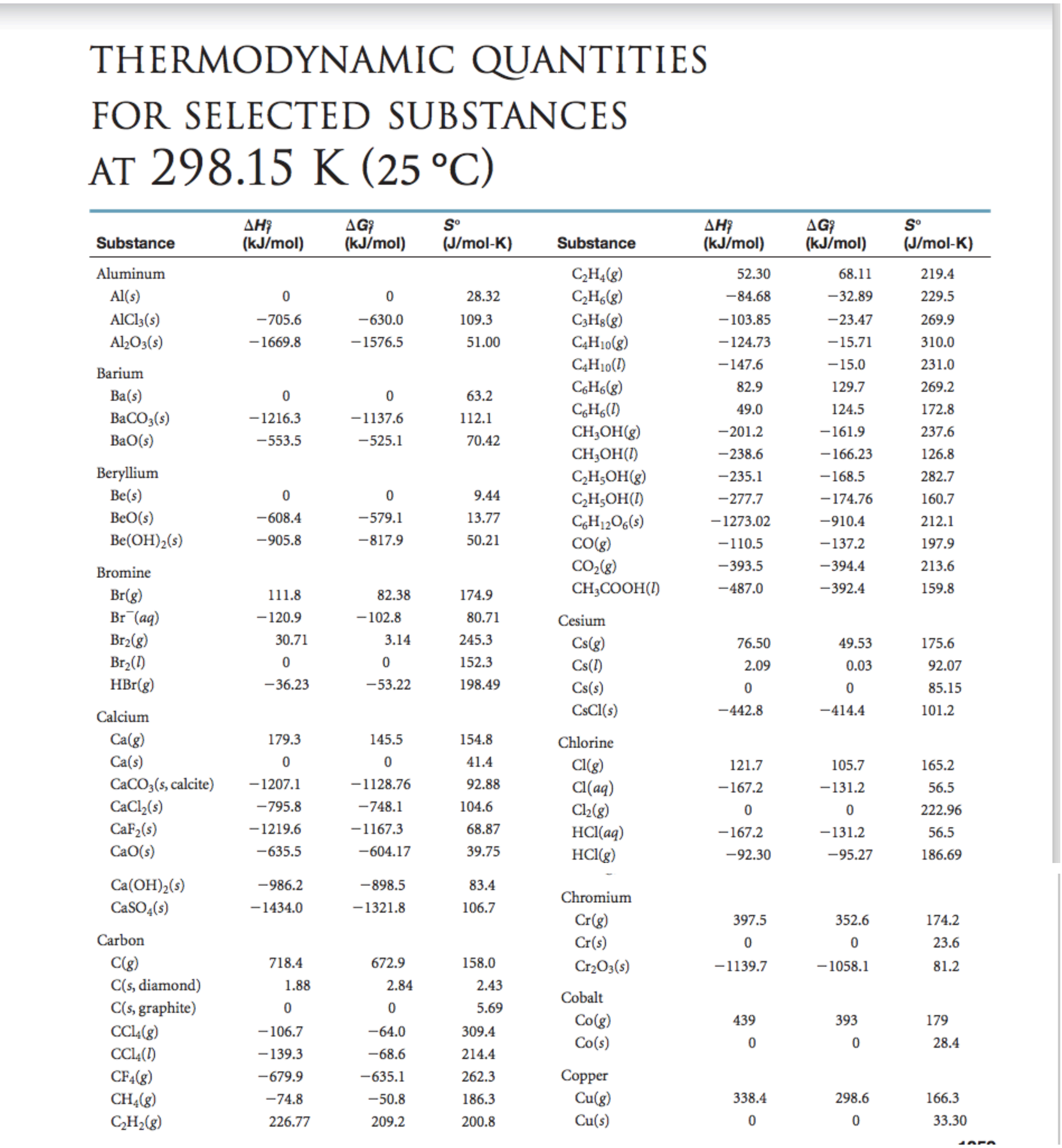
1. Thermodynamic Quantities for Selective Substances at 298 K

   This is where the standard values of Enthalpy of Formation, Gibbs Free Energy and Entropy can be found. This is essential in your study of Thermodynamics.

2. Standard Reduction Potentials at at 25°C

   This is where the standard values of Standard Reduction Potentials can be found. This is essential in your study of Electrochemistry.

Thermodynamic Quantities for Selective Substances at 298 K



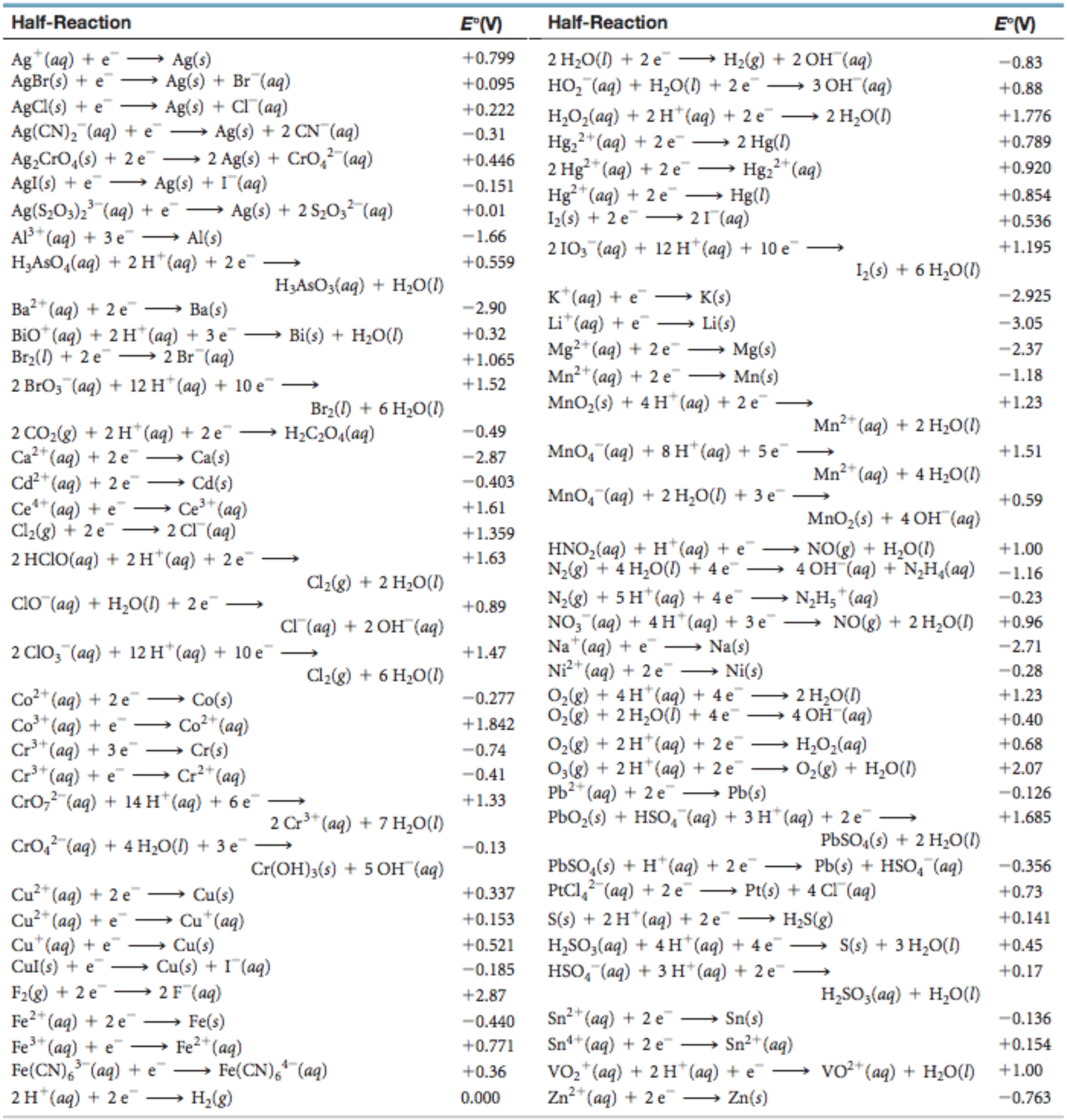
THERMODYNAMIC QUANTITIES FOR SELECTED SUBSTANCES AT 298.15 K (25 °C)

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol-K)
Aluminum			
$Al(s)$	0	0	28.32
$AlCl_3(s)$	−705.6	−630.0	109.3
$Al_2O_3(s)$	−1669.8	−1576.5	51.00
Barium			
$Ba(s)$	0	0	63.2
$BaCO_3(s)$	−1216.3	−1137.6	112.1
$BaO(s)$	−553.5	−525.1	70.42
Beryllium			
$Be(s)$	0	0	9.44
$BeO(s)$	−608.4	−579.1	13.77
$Be(OH)_2(s)$	−905.8	−817.9	50.21
Bromine			
$Br(g)$	111.8	82.38	174.9
$Br^-(aq)$	−120.9	−102.8	80.71
$Br_2(g)$	30.71	3.14	245.3
$Br_2(l)$	0	0	152.3
$HBr(g)$	−36.23	−53.22	198.49
Calcium			
$Ca(g)$	179.3	145.5	154.8
$Ca(s)$	0	0	41.4
$CaCO_3(s, \text{calcite})$	−1207.1	−1128.76	92.88
$CaCl_2(s)$	−795.8	−748.1	104.6
$CaF_2(s)$	−1219.6	−1167.3	68.87
$CaO(s)$	−635.5	−604.17	39.75
$Ca(OH)_2(s)$	−986.2	−898.5	83.4
$CaSO_4(s)$	−1434.0	−1321.8	106.7
Carbon			
$C(g)$	718.4	672.9	158.0
$C(s, \text{diamond})$	1.88	2.84	2.43
$C(s, \text{graphite})$	0	0	5.69
$CCl_4(g)$	−106.7	−64.0	309.4
$CCl_4(l)$	−139.3	−68.6	214.4
$CF_4(g)$	−679.9	−635.1	262.3
$CH_4(g)$	−74.8	−50.8	186.3
$C_2H_2(g)$	226.77	209.2	200.8
$C_2H_4(g)$	52.30	68.11	219.4
$C_2H_6(g)$	−84.68	−32.89	229.5
$C_3H_8(g)$	−103.85	−23.47	269.9
$C_4H_{10}(g)$	−124.73	−15.71	310.0
$C_4H_{10}(l)$	−147.6	−15.0	231.0
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_6(l)$	49.0	124.5	172.8
$CH_3OH(g)$	−201.2	−161.9	237.6
$CH_3OH(l)$	−238.6	−166.23	126.8
$C_2H_5OH(g)$	−235.1	−168.5	282.7
$C_2H_5OH(l)$	−277.7	−174.76	160.7
$C_6H_{12}O_6(s)$	−1273.02	−910.4	212.1
$CO(g)$	−110.5	−137.2	197.9
$CO_2(g)$	−393.5	−394.4	213.6
$CH_3COOH(l)$	−487.0	−392.4	159.8
Cesium			
$Cs(g)$	76.50	49.53	175.6
$Cs(l)$	2.09	0.03	92.07
$Cs(s)$	0	0	85.15
$CsCl(s)$	−442.8	−414.4	101.2
Chlorine			
$Cl(g)$	121.7	105.7	165.2
$Cl(aq)$	−167.2	−131.2	56.5
$Cl_2(g)$	0	0	222.96
$HCl(aq)$	−167.2	−131.2	56.5
$HCl(g)$	−92.30	−95.27	186.69
Chromium			
$Cr(g)$	397.5	352.6	174.2
$Cr(s)$	0	0	23.6
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
Cobalt			
$Co(g)$	439	393	179
$Co(s)$	0	0	28.4
Copper			
$Cu(g)$	338.4	298.6	166.3
$Cu(s)$	0	0	33.30

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol-K)
$CuCl_2(s)$	−205.9	−161.7	108.1
$CuO(s)$	−156.1	−128.3	42.59
$Cu_2O(s)$	−170.7	−147.9	92.36
Fluorine			
$F(g)$	80.0	61.9	158.7
$F(aq)$	−332.6	−278.8	−13.8
$F_2(g)$	0	0	202.7
$HF(g)$	−268.61	−270.70	173.51
Hydrogen			
$H(g)$	217.94	203.26	114.60
$H^+(aq)$	0	0	0
$H^+(g)$	1536.2	1517.0	108.9
$H_2(g)$	0	0	130.58
Iodine			
$I(g)$	106.60	70.16	180.66
$I^-(aq)$	−55.19	−51.57	111.3
$I_2(g)$	62.25	19.37	260.57
$I_2(s)$	0	0	116.73
$HI(g)$	25.94	1.30	206.3
Iron			
$Fe(g)$	415.5	369.8	180.5
$Fe(s)$	0	0	27.15
$Fe^{2+}(aq)$	−87.86	−84.93	113.4
$Fe^{3+}(aq)$	−47.69	−10.54	293.3
$FeCl_2(s)$	−341.8	−302.3	117.9
$FeCl_3(s)$	−400	−334	142.3
$FeO(s)$	−271.9	−255.2	60.75
$Fe_2O_3(s)$	−822.16	−740.98	89.96
$Fe_3O_4(s)$	−1117.1	−1014.2	146.4
$FeS_2(s)$	−171.5	−160.1	52.92
Lead			
$Pb(s)$	0	0	68.85
$PbBr_2(s)$	−277.4	−260.7	161
$PbCO_3(s)$	−699.1	−625.5	131.0
$Pb(NO_3)_2(aq)$	−421.3	−246.9	303.3
$Pb(NO_3)_2(s)$	−451.9	—	—
$PbO(s)$	−217.3	−187.9	68.70
Lithium			
$Li(g)$	159.3	126.6	138.8
$Li(s)$	0	0	29.09
$Li^+(aq)$	−278.5	−273.4	12.2
$Li^+(g)$	685.7	648.5	133.0
$LiCl(s)$	−408.3	−384.0	59.30
Magnesium			
$Mg(g)$	147.1	112.5	148.6
$Mg(s)$	0	0	32.51
$MgCl_2(s)$	−641.6	−592.1	89.6
$MgO(s)$	−601.8	−569.6	26.8
$Mg(OH)_2(s)$	−924.7	−833.7	63.24
Manganese			
$Mn(g)$	280.7	238.5	173.6
$Mn(s)$	0	0	32.0
$MnO(s)$	−385.2	−362.9	59.7
$MnO_2(s)$	−519.6	−464.8	53.14
$MnO_4^-(aq)$	−541.4	−447.2	191.2
Mercury			
$Hg(g)$	60.83	31.76	174.89
$Hg(l)$	0	0	77.40
$HgCl_2(s)$	−230.1	−184.0	144.5
$Hg_2Cl_2(s)$	−264.9	−210.5	192.5
Nickel			
$Ni(g)$	429.7	384.5	182.1
$Ni(s)$	0	0	29.9
$NiCl_2(s)$	−305.3	−259.0	97.65
$NiO(s)$	−239.7	−211.7	37.99
Nitrogen			
$N(g)$	472.7	455.5	153.3
$N_2(g)$	0	0	191.50
$NH_3(aq)$	−80.29	−26.50	111.3
$NH_3(g)$	−46.19	−16.66	192.5
$NH_4^+(aq)$	−132.5	−79.31	113.4
$N_2H_4(g)$	95.40	159.4	238.5
$NH_4CN(s)$	0.0	—	—
$NH_4Cl(s)$	−314.4	−203.0	94.6
$NH_4NO_3(s)$	−365.6	−184.0	151
$NO(g)$	90.37	86.71	210.62
$NO_2(g)$	33.84	51.84	240.45
$N_2O(g)$	81.6	103.59	220.0
$N_2O_4(g)$	9.66	98.28	304.3
$NOCl(g)$	52.6	66.3	264
$HNO_3(aq)$	−206.6	−110.5	146
$HNO_3(g)$	−134.3	−73.94	266.4
Oxygen			
$O(g)$	247.5	230.1	161.0
$O_2(g)$	0	0	205.0
$O_3(g)$	142.3	163.4	237.6
$OH^-(aq)$	−230.0	−157.3	−10.7
$H_2O(g)$	−241.82	−228.57	188.83
$H_2O(l)$	−285.83	−237.13	69.91
$H_2O_2(g)$	−136.10	−105.48	232.9
$H_2O_2(l)$	−187.8	−120.4	109.6
Phosphorus			
$P(g)$	316.4	280.0	163.2
$P_2(g)$	144.3	103.7	218.1

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol-K)
$P_4(g)$	58.9	24.4	280
$P_4(s, \text{red})$	−17.46	−12.03	22.85
$P_4(s, \text{white})$	0	0	41.08
$PCl_3(g)$	−288.07	−269.6	311.7
$PCl_3(l)$	−319.6	−272.4	217
$PF_5(g)$	−1594.4	−1520.7	300.8
$PH_3(g)$	5.4	13.4	210.2
$P_4O_6(s)$	−1640.1	—	—
$P_4O_{10}(s)$	−2940.1	−2675.2	228.9
$POCl_3(g)$	−542.2	−502.5	325
$POCl_3(l)$	−597.0	−520.9	222
$H_3PO_4(aq)$	−1288.3	−1142.6	158.2
Potassium			
$K(g)$	89.99	61.17	160.2
$K(s)$	0	0	64.67
$KCl(s)$	−435.9	−408.3	82.7
$KClO_3(s)$	−391.2	−289.9	143.0
$KClO_3(aq)$	−349.5	−284.9	265.7
$K_2CO_3(s)$	−1150.18	−1064.58	155.44
$KNO_3(s)$	−492.70	−393.13	132.9
$K_2O(s)$	−363.2	−322.1	94.14
$KO_2(s)$	−284.5	−240.6	122.5
$K_2O_2(s)$	−495.8	−429.8	113.0
$KOH(s)$	−424.7	−378.9	78.91
$KOH(aq)$	−482.4	−440.5	91.6
Rubidium			
$Rb(g)$	85.8	55.8	170.0
$Rb(s)$	0	0	76.78
$RbCl(s)$	−430.5	−412.0	92
$RbClO_3(s)$	−392.4	−292.0	152
Scandium			
$Sc(g)$	377.8	336.1	174.7
$Sc(s)$	0	0	34.6
Selenium			
$H_2Se(g)$	29.7	15.9	219.0
Silicon			
$Si(g)$	368.2	323.9	167.8
$Si(s)$	0	0	18.7
$SiC(s)$	−73.22	−70.85	16.61
$SiCl_4(l)$	−640.1	−572.8	239.3
$SiO_2(s, \text{quartz})$	−910.9	−856.5	41.84
Silver			
$Ag(s)$	0	0	42.55
$Ag^+(aq)$	105.90	77.11	73.93
$AgCl(s)$	−127.0	−109.70	96.11
$Ag_2O(s)$	−31.05	−11.20	121.3
$AgNO_3(s)$	−124.4	−33.41	140.9
Sodium			
$Na(g)$	107.7	77.3	153.7
$Na(s)$	0	0	51.45
$Na^+(aq)$	−240.1	−261.9	59.0
$Na^+(g)$	609.3	574.3	148.0
$NaBr(aq)$	−360.6	−364.7	141.00
$NaBr(s)$	−361.4	−349.3	86.82
$Na_2CO_3(s)$	−1130.9	−1047.7	136.0
$NaCl(aq)$	−407.1	−393.0	115.5
$NaCl(g)$	−181.4	−201.3	229.8
$NaCl(s)$	−410.9	−384.0	72.33
$NaHCO_3(s)$	−947.7	−851.8	102.1
$NaNO_3(aq)$	−446.2	−372.4	207
$NaNO_3(s)$	−467.9	−367.0	116.5
$NaOH(aq)$	−469.6	−419.2	49.8
$NaOH(s)$	−425.6	−379.5	64.46
$Na_2SO_4(s)$	−1387.1	−1270.2	149.6
Strontium			
$SrO(s)$	−592.0	−561.9	54.9
$Sr(g)$	164.4	110.0	164.6
Sulfur			
$S(s, \text{rhombic})$	0	0	31.88
$S_8(g)$	102.3	49.7	430.9
$SO_2(g)$	−296.9	−300.4	248.5
$SO_3(g)$	−395.2	−370.4	256.2
$SO_4^{2-}(aq)$	−909.3	−744.5	20.1
$SOCl_2(l)$	−245.6	—	—
$H_2S(g)$	−20.17	−33.01	205.6
$H_2SO_4(aq)$	−909.3	−744.5	20.1
$H_2SO_4(l)$	−814.0	−689.9	156.1
Titanium			
$Ti(g)$	468	422	180.3
$Ti(s)$	0	0	30.76
$TiCl_4(g)$	−763.2	−726.8	354.9
$TiCl_4(l)$	−804.2	−728.1	221.9
$TiO_2(s)$	−944.7	−889.4	50.29
Vanadium			
$V(g)$	514.2	453.1	182.2
$V(s)$	0	0	28.9
Zinc			
$Zn(g)$	130.7	95.2	160.9
$Zn(s)$	0	0	41.63
$ZnCl_2(s)$	−415.1	−369.4	111.5
$ZnO(s)$	−348.0	−318.2	43.9

Standard Reduction Potentials at at 25°C



Half-Reaction	E°(V)
$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$	+0.799
$AgBr(s) + e^{-} \longrightarrow Ag(s) + Br^{-}(aq)$	+0.095
$AgCl(s) + e^{-} \longrightarrow Ag(s) + Cl^{-}(aq)$	+0.222
$Ag(CN)_2^{-}(aq) + e^{-} \longrightarrow Ag(s) + 2\,CN^{-}(aq)$	−0.31
$Ag_2CrO_4(s) + 2\,e^{-} \longrightarrow 2\,Ag(s) + CrO_4^{2-}(aq)$	+0.446
$AgI(s) + e^{-} \longrightarrow Ag(s) + I^{-}(aq)$	−0.151
$Ag(S_2O_3)_2^{3-}(aq) + e^{-} \longrightarrow Ag(s) + 2\,S_2O_3^{2-}(aq)$	+0.01
$Al^{3+}(aq) + 3\,e^{-} \longrightarrow Al(s)$	−1.66
$H_3AsO_4(aq) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_3AsO_3(aq) + H_2O(l)$	+0.559
$Ba^{2+}(aq) + 2\,e^{-} \longrightarrow Ba(s)$	−2.90
$BiO^{+}(aq) + 2\,H^{+}(aq) + 3\,e^{-} \longrightarrow Bi(s) + H_2O(l)$	+0.32
$Br_2(l) + 2\,e^{-} \longrightarrow 2\,Br^{-}(aq)$	+1.065
$2\,BrO_3^{-}(aq) + 12\,H^{+}(aq) + 10\,e^{-} \longrightarrow Br_2(l) + 6\,H_2O(l)$	+1.52
$2\,CO_2(g) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2C_2O_4(aq)$	−0.49
$Ca^{2+}(aq) + 2\,e^{-} \longrightarrow Ca(s)$	−2.87
$Cd^{2+}(aq) + 2\,e^{-} \longrightarrow Cd(s)$	−0.403
$Ce^{4+}(aq) + e^{-} \longrightarrow Ce^{3+}(aq)$	+1.61
$Cl_2(g) + 2\,e^{-} \longrightarrow 2\,Cl^{-}(aq)$	+1.359
$2\,HClO(aq) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow Cl_2(g) + 2\,H_2O(l)$	+1.63
$ClO^{-}(aq) + H_2O(l) + 2\,e^{-} \longrightarrow Cl^{-}(aq) + 2\,OH^{-}(aq)$	+0.89
$2\,ClO_3^{-}(aq) + 12\,H^{+}(aq) + 10\,e^{-} \longrightarrow Cl_2(g) + 6\,H_2O(l)$	+1.47
$Co^{2+}(aq) + 2\,e^{-} \longrightarrow Co(s)$	−0.277
$Co^{3+}(aq) + e^{-} \longrightarrow Co^{2+}(aq)$	+1.842
$Cr^{3+}(aq) + 3\,e^{-} \longrightarrow Cr(s)$	−0.74
$Cr^{3+}(aq) + e^{-} \longrightarrow Cr^{2+}(aq)$	−0.41
$CrO_7^{2-}(aq) + 14\,H^{+}(aq) + 6\,e^{-} \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$CrO_4^{2-}(aq) + 4\,H_2O(l) + 3\,e^{-} \longrightarrow Cr(OH)_3(s) + 5\,OH^{-}(aq)$	−0.13
$Cu^{2+}(aq) + 2\,e^{-} \longrightarrow Cu(s)$	+0.337
$Cu^{2+}(aq) + e^{-} \longrightarrow Cu^{+}(aq)$	+0.153
$Cu^{+}(aq) + e^{-} \longrightarrow Cu(s)$	+0.521
$CuI(s) + e^{-} \longrightarrow Cu(s) + I^{-}(aq)$	−0.185
$F_2(g) + 2\,e^{-} \longrightarrow 2\,F^{-}(aq)$	+2.87
$Fe^{2+}(aq) + 2\,e^{-} \longrightarrow Fe(s)$	−0.440
$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$	+0.771
$Fe(CN)_6^{3-}(aq) + e^{-} \longrightarrow Fe(CN)_6^{4-}(aq)$	+0.36
$2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2(g)$	0.000
$2\,H_2O(l) + 2\,e^{-} \longrightarrow H_2(g) + 2\,OH^{-}(aq)$	−0.83
$HO_2^{-}(aq) + H_2O(l) + 2\,e^{-} \longrightarrow 3\,OH^{-}(aq)$	+0.88
$H_2O_2(aq) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow 2\,H_2O(l)$	+1.776
$Hg_2^{2+}(aq) + 2\,e^{-} \longrightarrow 2\,Hg(l)$	+0.789
$2\,Hg^{2+}(aq) + 2\,e^{-} \longrightarrow Hg_2^{2+}(aq)$	+0.920
$Hg^{2+}(aq) + 2\,e^{-} \longrightarrow Hg(l)$	+0.854
$I_2(s) + 2\,e^{-} \longrightarrow 2\,I^{-}(aq)$	+0.536
$2\,IO_3^{-}(aq) + 12\,H^{+}(aq) + 10\,e^{-} \longrightarrow I_2(s) + 6\,H_2O(l)$	+1.195
$K^{+}(aq) + e^{-} \longrightarrow K(s)$	−2.925
$Li^{+}(aq) + e^{-} \longrightarrow Li(s)$	−3.05
$Mg^{2+}(aq) + 2\,e^{-} \longrightarrow Mg(s)$	−2.37
$Mn^{2+}(aq) + 2\,e^{-} \longrightarrow Mn(s)$	−1.18
$MnO_2(s) + 4\,H^{+}(aq) + 2\,e^{-} \longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	+1.23
$MnO_4^{-}(aq) + 8\,H^{+}(aq) + 5\,e^{-} \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
$MnO_4^{-}(aq) + 2\,H_2O(l) + 3\,e^{-} \longrightarrow MnO_2(s) + 4\,OH^{-}(aq)$	+0.59
$HNO_2(aq) + H^{+}(aq) + e^{-} \longrightarrow NO(g) + H_2O(l)$	+1.00
$N_2(g) + 4\,H_2O(l) + 4\,e^{-} \longrightarrow 4\,OH^{-}(aq) + N_2H_4(aq)$	−1.16
$N_2(g) + 5\,H^{+}(aq) + 4\,e^{-} \longrightarrow N_2H_5^{+}(aq)$	−0.23
$NO_3^{-}(aq) + 4\,H^{+}(aq) + 3\,e^{-} \longrightarrow NO(g) + 2\,H_2O(l)$	+0.96
$Na^{+}(aq) + e^{-} \longrightarrow Na(s)$	−2.71
$Ni^{2+}(aq) + 2\,e^{-} \longrightarrow Ni(s)$	−0.28
$O_2(g) + 4\,H^{+}(aq) + 4\,e^{-} \longrightarrow 2\,H_2O(l)$	+1.23
$O_2(g) + 2\,H_2O(l) + 4\,e^{-} \longrightarrow 4\,OH^{-}(aq)$	+0.40
$O_2(g) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2O_2(aq)$	+0.68
$O_3(g) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow O_2(g) + H_2O(l)$	+2.07
$Pb^{2+}(aq) + 2\,e^{-} \longrightarrow Pb(s)$	−0.126
$PbO_2(s) + HSO_4^{-}(aq) + 3\,H^{+}(aq) + 2\,e^{-} \longrightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.685
$PbSO_4(s) + H^{+}(aq) + 2\,e^{-} \longrightarrow Pb(s) + HSO_4^{-}(aq)$	−0.356
$PtCl_4^{2-}(aq) + 2\,e^{-} \longrightarrow Pt(s) + 4\,Cl^{-}(aq)$	+0.73
$S(s) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2S(g)$	+0.141
$H_2SO_3(aq) + 4\,H^{+}(aq) + 4\,e^{-} \longrightarrow S(s) + 3\,H_2O(l)$	+0.45
$HSO_4^{-}(aq) + 3\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2SO_3(aq) + H_2O(l)$	+0.17
$Sn^{2+}(aq) + 2\,e^{-} \longrightarrow Sn(s)$	−0.136
$Sn^{4+}(aq) + 2\,e^{-} \longrightarrow Sn^{2+}(aq)$	+0.154
$VO_2^{+}(aq) + 2\,H^{+}(aq) + e^{-} \longrightarrow VO^{2+}(aq) + H_2O(l)$	+1.00
$Zn^{2+}(aq) + 2\,e^{-} \longrightarrow Zn(s)$	−0.763