INTRODUCTORY CHEMISTRY 2

Dr Dejene Ayele Tessema
Foreword

The African Virtual University (AVU) is proud to participate in increasing access to education in African countries through the production of quality learning materials. We are also proud to contribute to global knowledge as our Open Educational Resources (OERs) are mostly accessed from outside the African continent. This module was prepared in collaboration with twenty one (21) African partner institutions which participated in the AVU Multinational Project I and II.

From 2005 to 2011, an ICT-integrated Teacher Education Program, funded by the African Development Bank, was developed and offered by 12 universities drawn from 10 countries which worked collaboratively to design, develop, and deliver their own Open Distance and e-Learning (ODeL) programs for teachers in Biology, Chemistry, Physics, Math, ICTs for teachers, and Teacher Education Professional Development. Four Bachelors of Education in mathematics and sciences were developed and peer-reviewed by African Subject Matter Experts (SMEs) from the participating institutions. A total of 73 modules were developed and translated to ensure availability in English, French and Portuguese making it a total of 219 modules. These modules have also been made available as Open Educational Resources (OER) on oer.avu.org, and have since then been accessed over 2 million times.

In 2012 a second phase of this project was launched to build on the existing teacher education modules, learning from the lessons of the existing teacher education program, reviewing the existing modules and creating new ones. This exercise was completed in 2017.

On behalf of the African Virtual University and our patron, our partner institutions, the African Development Bank, I invite you to use this module in your institution, for your own education, to share it as widely as possible, and to participate actively in the AVU communities of practice of your interest. We are committed to be on the frontline of developing and sharing open educational resources.

The African Virtual University (AVU) is a Pan African Intergovernmental Organization established by charter with the mandate of significantly increasing access to quality higher education and training through the innovative use of information communication technologies. A Charter, establishing the AVU as an Intergovernmental Organization, has been signed so far by nineteen (19) African Governments - Kenya, Senegal, Mauritania, Mali, Cote d’Ivoire, Tanzania, Mozambique, Democratic Republic of Congo, Benin, Ghana, Republic of Guinea, Burkina Faso, Niger, South Sudan, Sudan, The Gambia, Guinea-Bissau, Ethiopia and Cape Verde.

The following institutions participated in the teacher education program of the Multinational Project I: University of Nairobi – Kenya, Kyambogo University – Uganda, Open University of Tanzania, University of Zambia, University of Zimbabwe – Zimbabwe, Jimma University – Ethiopia, Amoud University - Somalia; Université Cheikh Anta Diop (UCAD)-Senegal, Université d’ Antananarivo – Madagascar, Universidade Pedagogica – Mozambique, East African University - Somalia, and University of Hargeisa - Somalia
The following institutions participated in the teacher education program of the Multinational Project II: University of Juba (UOJ) - South Sudan, University of The Gambia (UTG), University of Port Harcourt (UNIPORT) – Nigeria, Open University of Sudan (OUS) – Sudan, University of Education Winneba (UEW) – Ghana, University of Cape Verde (UniCV) – Cape Verde, Institut des Sciences (IDS) – Burkina Faso, Ecole Normale Supérieure (ENSUP) - Mali, Université Abdou Moumouni (UAM) - Niger, Institut Supérieur Pédagogique de la Gombe (ISPG) – Democratic Republic of Congo and Escola Normal Superior Tchicote – Guinea Bissau

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The Rector

African Virtual University
Production Credits

This second edition is the result of the revision of the first edition of this module. The informations provided below, at the exception of the name of the author of the first edition, refer to the second edition.

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- Unit II: Solutions and their Properties  
- Unit III: Energy and Chemical Reactions  
- Unit IV: Introduction to Organic Chemistry  

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Unit 1: Chemical Reaction rates and Equilibrium (30 hrs)  
Unit 2: Physical properties of Solutions  
Unit 3: Energy and Chemical Reactions  
Unit 4: Introduction to organic chemistry  

Introduction to Chemistry  

General Objective(s)  
Unit I: Chemical Reaction Rates and Equilibrium.  
Unit II: Solutions and their Properties  
Unit III: Energy and Chemical Reactions  
Unit IV: Introduction to Organic Chemistry  

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Introductory General Chemistry

Unit I: Chemical Reaction Rates and Equilibrium

Unit II: Solutions and their Properties

Unit III: Energy and Chemical Reactions

Unit IV: Introduction to Organic Chemistry

Time

120 hours (20 more)

- Unit 1: Chemical Reaction rates and Equilibrium (30 hrs)
- Unit 2: Physical properties of Solutions (30 hrs)
- Unit 3: Energy and Chemical Reactions (25 hrs)
- Unit 4: Introduction to organic chemistry (15 hrs)

Materials

Tools and resources:

You will require the following tools and resources for completing this module

Computer, CD-ROMs, and e-library

To access this module, exams, and other relevant materials on a computer

Internet

To access the module and other suggested reference materials.

For interactive discussions/chat sessions

Recommended textbooks and reference materials

To assist learning and further understanding of the topics in the module
Module Rationale

This module is the second half of the basic first year University course in chemistry. In the first half of the basic first year course i.e., General chemistry, module 1, we examined the concepts that underpin matter and measurement, atomic structure and periodicity. In this module we will look more closely at chemical reactions and the energy laws that govern them.

Most chemical reactions and virtually all biological processes take place not between pure solids, liquids or gases, but rather among ions and molecules dissolved in water or other solvents (i.e. in solution). In this module we will therefore examine the various types of solutions and their properties and discuss some introductory aspects of organic chemistry.

Overview

This module outlines some of the basic concepts in general chemistry. Typically it deals with chemical reactions and the energy changes that accompany such reactions. The module will therefore focus on the rates of chemical reactions, (i.e. how fast a reaction takes place) and the factors that affect reaction rates. Also the types and properties of solutions will be presented, concentrating mainly on intermolecular forces in solubility and their concentration units. Finally the module provides an overview of the classes of organic compounds, their nomenclature and functional groups.
Outline

Unit 1: Chemical Reaction rates and Equilibrium (30 hrs)

Reaction rate and Equilibrium (15 hrs)

- The rate of a reaction
- Factors affecting reaction rates
- Concentration dependence of rate: order of a reaction
- Determining reaction orders
- Determining reaction orders

Chemical equilibrium (15 hrs)

- Reversible reactions
- Law of chemical equilibrium
- Heterogeneous equilibria
- Factors affecting chemical equilibrium (Le-Chatelier’s Principle)

Unit 2: Physical properties of Solutions (30 hrs)

Solutions

- Types of solutions and the solution process
- Heats of solutions
- Solubility
- Effect of temperature on solubility
- Effect of pressure on solubility
- Concentration units
- Comparison of concentration units
- Colligative properties of solutions
Unit 3: Energy and Chemical Reactions (25 hrs)

Energy and chemical reactions

- Energy changes
- Enthalpy
- Enthalpy changes in chemical reactions
- Representing exothermic and endothermic reactions
- Stoichiometry and thermochemical reactions

Unit 4: Introduction to organic chemistry (15 hrs)

Introduction to organic chemistry

- Alkanes, Alkenes, and Alkynes
- IUPAC nomenclature of simple organic compounds
- Functional groups
Introduction to Chemistry

General Objective(s)

The general objective of the module is to acquaint you with the fundamental concepts and principles associated with chemical reactions notably their rates of reaction, how they are investigated and in particular, the factors including energy considerations that affect the different rates of reactions. The module will look at the physical properties of solutions, and the intermolecular forces that affect solubility including their concentration units. An introduction to the chemistry of carbon is included which is expected to provide the basis for more advanced work in organic chemistry in the years ahead.

Specific Learning Objectives (Instructional Objectives)
Unit I: Chemical Reaction Rates and Equilibrium

At the end of the unit the student should be able to:

- Write and interpret a rate law
- State and explain factors that control reaction rates
- Distinguish between reversible and irreversible reactions
- Use Le-Chatelier’s principle to determine shifts in equilibrium
- Calculate equilibrium constants and concentrations

Unit II: Solutions and their Properties

At the end of this learning activity the student should be able to:

- Describe the various types of solutions
- Define the various types of concentration units
- Calculate the concentrations of solutions by using the various concentration units
- Define solubility and describe how temperature and pressure affect solubility
- Describe colligative properties of non-electrolyte and electrolyte solutions

Unit III: Energy and Chemical Reactions

At the end of this learning activity the student should be able to:

- State and explain the law of conservation of energy
- Explain energy change during a chemical reaction and draw energy diagrams for the transfer of energy between a system and its surroundings.
- Draw energy profiles of exothermic and endothermic reactions
- Do stoichiometric calculations in thermochemical reactions

Unit IV: Introduction to Organic Chemistry

At the end of this learning activity you should be able to:

- Describe the class of organic compounds known as hydrocarbons.
- Write structural formulae and isomers of organic compounds
- Name different classes of organic compounds using IUPAC nomenclature
- Distinguish compounds based on their functional groups
Teaching and Learning Activities

Pre-assessment

Title of pre-assessment: A pre-test for General Chemistry 2

Rationale: This test is intended to assess the level of your existing chemistry knowledge, which is a prerequisite for successful learning of this module.

Questions

1. When pure compounds or elements are mixed in any proportion the product will be,
   a) a mixture    b) a pure compound    c) an element    d) a substance

2. A homogenous mixture is similar to a heterogenous mixture in that,
   a) both of them have definite composition
   b) both of them do not have definite composition
   c) both of them have uniform composition
   d) both of them are formed by the chemical combination of two or more pure substances

3. The chemical combination of three different kinds of atoms results in the formation of
   a) a single large atom    c) a molecule
   b) an element    d) a compound

4. Which of the following is correct about heat and temperature?
   a) Samples of the same substance at the same temperature will have the same heat content irrespective of their mass.
   b) Two samples of different substances which have the same mass and temperature will have the same heat content.
   c) All substances having the same temperature will have the same heat content.
   d) If the heat content of two substances with the same mass is the same they must have the same specific heat capacity.
5. Which of the following properties of solutions is a colligative property?
   a) viscosity  c) Osmotic pressure
   b) Heat of a solution.  d) Solubility

6. In reversible reactions
   a) the concentration of the products and the reactants will be equal when the reaction reaches equilibrium
   b) half of the initial concentration of the reactants will be left un-reacted at equilibrium
   c) the rates of the forward and the reverse reactions will be the same at equilibrium.
   d) the forward reaction is slower than the reverse reaction rate before equilibrium and faster after equilibrium

7. The fact that the solubility of a given salt in water increases with an increase in temperature implies that:
   a) the solution process is exothermic.
   b) the solution process is endothermic.
   c) the energy possessed by the solution is less than the energy possessed by the components of the solution before they were mixed
   d) the solution process is neither endothermic nor exothermic

Answer questions 8 and 9 based on the hypothetical equation, $2A + 2B \rightleftharpoons 2C + D$, which is exothermic in the forward direction and all reactants and products are gasses.

8. An increase pressure
   a) shifts the equilibrium to the right
   b) shifts the equilibrium to the left
   c) decreases the value of Ke
   d) will have no effect on the position of the equilibrium

9. A decrease in temperature
   a) shifts the equilibrium to the left
   b) shifts the equilibrium to the right
   c) will have no effect on the equilibrium position.
d) will decrease the equilibrium constant value

10. Organic chemistry deals with the chemistry of
a) carbon compounds
b) hydrocarbons only
c) aliphatic compounds only
d) inorganic elements

11. The IUPAC name for the compound, CH₃-CH₂-CH₂-CH-CH₃, is

\[
\text{CH}_3
\]

a) 2-methyl butane  

b) 2-methyl pentane  

c) 2-methyl hexane  

d) 4-methyl pentane

12. The structural formula for 2-methyl butane is

\[
\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_-\text{CH}_3
\]

a) CH₃-CH₂-CH₂-CH-CH₃  

b) CH₃-CH₂-CH₂-CH-CH₃  

c) CH₃-CH-CH₃  

d) CH₃-CH-CH₂-CH₃

13. Which of the following compounds contains an alcoholic functional group?

a) CH₃-CO-CH₃  

b) CH₃-CH₂-OH  

c) CH₃CH₂CHO  

d) CH₃-O-CH₃

14. Hydrocarbons are compounds which are made up of

Hydrogen, oxygen, nitrogen and carbon
Hydrogen, oxygen, and carbon
Hydrogen and carbon only
Hydrogen, carbon, sulfur, oxygen, nitrogen and carbon

15. Hydrocarbons which contain double bonds in their structure are known as,

a) alkanes  

b) alkynes  

c) cycloalkanes  

d) alkenes
### Teaching and Learning Activities

16. Alkanes have the general formula
   a) C\(_n\)H\(_{2n+1}\)  b) C\(_n\)H\(_{2n}\)  c) C\(_n\)H\(_{2n-2}\)  d) C\(_n\)H\(_{2n+2}\)

17. What is the molarity of a solution made by dissolving 20.0 g of NaOH in sufficient water to yield a 482 cm\(^3\) solution
   a) 1.04 M  b) 0.5 M  c) 2.04 M  d) 0.25 M

18. The molarity of a 0.15 N H\(_2\)SO\(_4\) solution is,
   a) 3.0 M  b) 0.075 M  c) 0.3 M  d) 0.25 M

19. The rate of a chemical reaction may be influenced by
   a) the concentration of the reactants
   b) the physical nature of the reactants
   c) the presence of a catalyst
   d) all of the above

20. A change in pressure will show a significant effect on the solubility of which type of solution?
   a) solid-liquid  b) gas-gas  c) liquid-liquid  d) solid-solid

### Answers

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### KEY CONCEPTS (GLOSSARY)

**Activation energy:** The minimum amount of energy required to initiate a chemical reaction.

**Alkanes:** Hydrocarbons having the general formula $C_nH_{2n+2}$, where $n = 1$.

**Alkenes:** Hydrocarbons that contain one or more carbon-carbon double bonds. They have the general formula $C_nH_{2n}$, where $n = 2, 3 \ldots$

**Alkynes:** Hydrocarbons that contain one or more carbon-carbon triple bonds. They have the general formula $C_nH_{2n-2}$, where $n = 2, 3 \ldots$

**Bond dissociation energy:** The enthalpy change required to break a particular bond in a mole of gaseous diatomic molecule.

**Born-Haber cycle:** The cycle that relates lattice energies of ionic compounds to ionization energies, electron affinities, heats of sublimation and formation, and bond dissociation energies.

**Chemical energy:** Energy stored within the structural units of chemical substances.

**Chemical Equilibrium:** A chemical state in which no net change can be observed.

**Colligative properties:** Properties of solutions which depend on the number of solute particles in solution and not on the nature of the solute particles.

**Concentration of a solution:** The amount of solute present per unit volume of the solution.

**Dynamic equilibrium:** An equilibrium in which a reaction proceeds both in the forward and reverse directions at exactly the same rate.

**Endothermic process:** A process in which heat is absorbed from the surrounding.

**Enthalpy:** A thermodynamic quantity used to describe heat changes taking place at constant pressure.

**Exothermic process:** A process in which heat is given off to the surrounding.

**First-order reaction:** A reaction whose rate depends on reactant concentration raised to the first power.

**Functional group:** part of a molecule having a special arrangement of atoms that is largely responsible for the chemical behavior of the parent molecule.

**Heat of solution:** is then defined as the quantity of energy that is absorbed or released when a solution is formed.
Heterogeneous mixture: A mixture in which components are not in the same phase.

Homogeneous mixture: A mixture in which components are in the same phase.

Hydrocarbons: Compounds made up of carbon and hydrogen only.

Le Chatelier’s principle: A principle which indicates that a system at equilibrium will adjust itself in such a way as to partially offset the stress when it is subjected to an external stress.

Rate constant: Constant of proportionality between the reaction rate and the concentration of reactants.

Rate law: An expression relating the rate of a reaction to the rate constant and the concentration of the reactants.

Reaction rate: The change in the concentration of reactant or product with time.

Reversible reaction: A reaction that can occur in both forward and reverse directions.

COMPULSORY READINGS

Complete reference:

Solutions: From Wikipedia, the free encyclopediad

http://en.wikipedia.org/wiki/Solutions

Abstract:

The article addresses most of the relevant concepts in solutions. The differences between a solution and a heterogeneous mixture, the intermolecular forces or attractions that hold molecules together including solvation, types of solutions, the effect of temperature and pressure on solubility, and the various concentration units are discussed. Coligative properties of solutions are briefly explained and the article provides links for further reference.

Rationale:

This article helps to provide the basis for further reading on the topic of solutions. It gives useful links to those concepts which are not discussed in detail in the article. Therefore, it is a useful article to study topics which will be discussed under the unit for solutions.
Complete reference:

Reaction Rate: From Wikipedia, the free encyclopedia

http://en.wikipedia.org/wiki/Reaction_rate

Chemical Equilibrium: http://en.wikipedia.org/wiki/Chemical_equilibrium

Abstract:

The article on reaction rate provides important discussions on the topic itself with emphasis on the rate equation, and the factors influencing reaction rate, notably, concentration, temperature, nature of reactants, pressure, and catalyst.

The article on chemical equilibrium focuses on the equilibrium conditions of reversible reactions. It defines and explains the differences between reversible and irreversible reactions and the conditions for chemical equilibrium based on Le-Chateliers principle.

Rationale:

The two links will help you as additional study materials for the unit ‘Reaction Rate and Equilibrium’ which is covered in this module. The articles in the two links present relevant and practical examples which will strengthen your conceptual and computational skills in the topics covered.

Organic Compounds: Naming and Isomerism

COMPULSORY RESOURCES

Two relevant images must be inserted here.

Resource #1

Complete reference: CD accompanying this module.

PDF files

1. 6-Naming&Isomerism
2. 10-CarbonylFunGroups
3. 59-MeasRxnRates
4. 60-StudyingRxnRates
5. 71-RecognizingEquilibrium
6. Solutions
Abstract:
The above files provide reading materials which help the student as supplementary resource material to study this module.

Rationale:
The resource materials provide relevant explanations on concepts covered in the units covered in this module: Chemical Reaction Rates and Equilibrium, Solutions and their Properties, Energy and Chemical Reactions and Introduction to Organic Chemistry. Exercises which should be worked out by students are also provided in the included materials.

Resource #2
Complete reference: MPEG file cdlab1 in accompanying CD

Abstract:
This multimedia resource is to be used by the student in studying the chapter ‘Chemical Reaction Rates and Equilibrium’ to get a clear idea on the concept of chemical equilibrium.

Rationale:
The multimedia resource material provides a useful demonstration of the equilibria occurring in a chromate-dichromate system.
Useful Links

Useful Link #1
Title: The Catalyst: Chemistry Resources For Teachers
URL: http://www.thecatalyst.org

DESCRIPTION
WELCOME to The Catalyst! This site has been developed specifically for the secondary education/high school level teacher, as a resource for finding relevant information for use in the teaching of chemistry and alternative education. Moreover, students and other visitors interested in the topic of chemistry will find The Catalyst to be a valuable web resource for finding the information or answers they are seeking, and are encouraged to take advantage of this site as well. This site is updated frequently, so stop by often. Thank you for visiting!

RATIONALE
Students are advised to visit this link because it provides relevant readings which are useful in strengthening the students understanding of the topics on chemical equilibrium, reaction rates and the factors affecting reaction rates. It also provides a clear explanation on exothermic and endothermic processes in reactions.

Useful Link #2
Title: Science Resource Center
URL: http://chem.lapeer.org

DESCRIPTION
This web site is for science teachers to share ideas. It provides labs, demonstrations, and other important information which teachers can access. The website grant to use and reproduce all materials at the site as long as the activities are not sold.

RATIONALE
This is a useful link because it provides study notes, worked examples and exercises on solutions, kinetics, and organic chemistry. The tests are accompanied by answers. Students should attempt these tests in order to assess their existing ability.
Useful Links # 3

Title: Chemistry Teaching Web Sites

URL: http://chem.lapeer.org/

DESCRIPTION

Reaction rate and equilibrium, properties of solutions, introductory organic chemistry, are extensively covered in this web site. The website also provides worked examples on each of the topics it discusses. This will give a good reference material on the topics discussed in this module. In addition, the web site helps students to find useful links for further reference.

RATIONALE

As a distance e-learner you are not able to get laboratory access for most of the experiments which should be ‘hands on’. This site is very essential to you in that it provides demonstrations and laboratory investigations some of which you can practice at home following the procedure provided. All the topics covered in this module are discussed in this site. Each of the demonstrations and laboratory investigations are accompanied by clearly stated objectives, a brief discussion, the steps to follow in carrying out the practice and questions which are designed to test your understanding of the subject. The site also provides exercises which cover all relevant points in a topic followed by their answers which will help you get feedback on your understanding of the topics.

Useful link # 4

Title: Chemistry Portfolio - Teaching and Learning

http://www.csus.edu/portfolio/prog/chem/Teach.stm

DESCRIPTION

As a future teacher it is quite necessary that you should know the modern world requirements of a good teacher on course delivering, assessment, course design and planning. This website provides important information on how to establish specific learning goals and expectations for students, designing courses, keeping up-to-date on relevant knowledge, and reflecting on teaching in order to improve student learning.

RATIONALE

In these pages you will be able to access information about assessment plan and how to handle assessment data.
As a future teacher you should be able to understand what knowledge level is expected from your students, the assessment method that you should apply and so on. Examples of students work are provided in this site. They will help you design activities for your future students.

**Useful link # 5**

**Title:** Introduction to Chemistry  
**URL:** [http://library.thinkquest.org](http://library.thinkquest.org)

**DESCRIPTION**
This site extensively covers all topics of introductory chemistry that would be covered in a first year chemistry course. The site provides suggestion on the order of viewing the site but you can select any topic that you wish to learn about.

**RATIONALE**
This website provides relevant reading materials and exercises on the topics covered in this module. It also links you to other websites such as Chempire and The Chem Files which give detailed explanations on: basic organic chemistry, solutions and concentration units, chemical equilibrium and chemical kinetics. The sites are easy to navigate, with topics divided into chapters giving more detailed explanations. Each section contains a glossary of terms and a quiz to apply what you have learned.

**Useful link # 6**

**Title:** Solutions  

**DESCRIPTION**
This website provides a brief but useful description on solutions. Definitions of terms like solute, solvent, solvation, saturated solution, unsaturated and supersaturated solutions, and solubility are given. The various kinds of solutions and the conditions that affect solubility are also discussed. The page also discusses the concept behind the solubilization process by taking into account solute-solvent polarity.
RATIONALE

This website provides relevant reading materials on the topic solutions. In addition to the brief and useful discussions provided in the page, it also links the student to other web pages that discuss in detail the concepts mentioned in the page.

You will find the links:

http://en.wikipedia.org/wiki/Concentration,

http://en.wikipedia.org/wiki/Solubility,

http://en.wikipedia.org/wiki/Solvent,

provided in this webpage to be very important to study the major concepts discussed in Unit II: Solutions and their Properties, of this module.

Useful link # 7

Title: Chemical Kinetics

URL: http://en.wikipedia.org/wiki/Chemical_kinetics

DESCRIPTION

This site extensively covers all topics of introductory chemistry that would be covered in a first year chemistry course. The site provides suggestion on the order of viewing the site but you can select any topic that you wish to learn about.

RATIONALE

The site provides excellent reading materials which will help the student to study the chapter on ‘Energy and Chemical Reactions’. In addition to relevant reading materials, explorer and master quizzes which will help the student to make self assessment on the above unit are given in the page.

Useful link # 8

Title: Chemistry @Davidson (Experiments and Exercises)

URL: http://www.chm.davidson.edu/chemistryApplets/index.html
DESCRIPTION

Experiments and exercises which cover all the topics discussed are provided in this webpage. The webpage contains wide range of topics in general chemistry which are well presented and easy to access. Students can choose and easily access relevant experiments and exercises to this module.

RATIONALE

This website provides extremely important experiments and exercises to the units covered in this module. Each experiment is proceeded by a brief description on the core concept behind that experiment and description of the activity. All the experiments given are followed by exercises which assist the student to evaluate his level of conceptual understanding.

Useful link # 9

Title: Chemistry: The Science in Context
URL: http://www.wwnorton.com/chemistry/concepts/ch16.htm

Description:

Chemistry: The Science in Context” is an online text material. It provides chapters which cover most topics in general chemistry. Chapter 5 – Solution Chemistry and the Hydrosphere, Chapter 11- Thermochemistry and the Quest for Energy, Chapter 13- Entropy and Free Energy and the Human Engine, Chapter 14 – Chemical Kinetics and Air Pollution, Chapter 16 Equilibrium in the aqueous Phase and Acid rain are the most relevant chapters to the topics covered in this module.

Rationale:

The reading materials provided in this website are very important and relevant to study the subject matter covered in the outline of this module. Students can access clearly presented materials which discuss core concepts in solutions, chemical equilibria, and energy changes accompanying chemical reactions. The contents of the material are well organized and could be accessed easily. All subtopics are followed by sample problems, exercises, tutorials and quizzes.
Useful Link # 10

Title: Virtual Textbook of Organic Chemistry

URL: http://www.cem.msu.edu/~reusch/VirtualText/intro1.htm

DESCRIPTION

This site is useful to be used as a reading material for the unit ‘Introductory Organic Chemistry’. All concepts covered in the unit are elaborated extensively in this webpage.

RATIONALE

This website provides useful and relevant reading materials for the Introductory Organic Chemistry unit covered in this module. Classification and nomenclature of hydrocarbons, functional groups and their properties are discussed very well. Subtopics are accompanied by practice problems which help the student to evaluate his concept understanding level. The website also contains links that provide nice collections of problems and answers.
Learning Activities

Learning activity 1

Title of Learning Activity: Reaction rate and equilibrium

Specific Teaching and Learning Objectives:

At the end of this learning activity you should be able to:

- Write and interpret a rate law
- Identify and explain factors that affect reaction rates
- Predict how changes in the conditions affect the rate of a reaction
- Predict the behaviour of an equilibrium system once it has been formed
- Use Le Chatelier’s principle to predict shifts in equilibrium
- Carry out calculations using the values of equilibrium constants

Summary of the learning activity:

This learning activity is the first unit to be covered in this module. The topics in this unit include reaction rates, order of a reaction, the factors that affect reaction rates and chemical equilibrium. At the end of each topic worked examples are given to provide a clear consistent methodology that you can follow to develop conceptual and quantitative problem solving skills. There are exercises that you will be required to work through, on completing your various readings.

List of relevant readings:

- Solutions in http://chemmovies.unl.edu/ChemAnime/index.htm
List of relevant resources:

- Computer with Internet facility to access links and relevant copy-write free resources.
- CD-Rom accompanying this module for compulsory readings and demonstrations.
- Multimedia resources like video, VCD and CD players.

List of relevant useful links:

- Understanding Chemistry, by Jim Clark (Chapter on physical chemistry covers rates of reactions, and chemical equilibria).
- ScienceWorld, by Eric Weisstein (Chapter on chemical reactions covers reaction energy, reaction pathways and reaction properties)

In the links given below you will find discussions on rate equilibria and exams which you have to try and assess to what extent you have grasped the concepts which are discussed in this unit and your ability to solve related problems. You are advised to check your answers against the answers provided after you have attempted all the questions. Doing so will help you identify the concepts which you haven’t understood well and which you need to work on more.


Detailed description of the activity:
In your first general chemistry module (Introductory General Chemistry I) you learnt that a balanced chemical equation is a chemical statement that gives the mole ratios of reactants and products as well as the ratios of formula units. A balanced chemical equation as ordinarily written provides valuable chemical information as to the masses, or volumes (if gases are involved) and is therefore an essential quantitative tool for calculating product yields from amounts of reacting substances. However, a balanced chemical equation tells us nothing about how fast or quickly chemical changes occur, or what energy changes are associated with the molecular interaction in a given chemical reaction. Knowing how quickly a chemical reaction occurs is a crucial factor in how the reaction affects its surroundings. Therefore, knowing the rate of a chemical reaction and the energy changes associated with the molecular interaction during the reaction are integral to understanding the reaction.

The questions of “how fast does the reaction go”? and ‘what conditions or factors bring about variations in speed’? What are the energy changes associated with the molecular interaction in a given chemical reaction are the subject of this unit.

The unit mainly focuses on the speed (rate) of a reaction, the stepwise changes reactants undergo in their conversion to products, in reversible and irreversible reactions; the condition of chemical equilibrium and the application of Le -Chatelier’s principle in the rate of reaction. We will now start our discussion by defining rate of a reaction and then we will see the mathematical expressions of reaction rates.

The concept of rate applies to a number of phenomenon in our daily life. For example the change in distance by an athlete over time is the running rate of the athlete. The number of soap bars that are produced in a given time is the rate of production of soap etc. We apply the same principle in chemical reaction. This time as products are formed reactants are used up and rate (speed) of a chemical reaction can be expressed as the ratio of the change in the concentration of a reactant (or product) to a change in time. The study that deals with the movement/motion-the speeds, or rates of chemical reactions is known as chemical kinetics.

Consider the following hypothetical reaction between reactants A and B to form products C and D

\[ aA + bB \rightarrow cC + dD \] .................................1.1

(a, b, c and d are the stoichiometric coefficients of A, B, C, and D respectively)

The rate of this reaction is the speed at which A or B is consumed or, alternatively, the speed at which C or D is formed. Mathematically this is given by

\[
\text{Rate} = \frac{-1}{a} \frac{\Delta[A]}{\Delta t} = \frac{-1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} \] .................................1.2

\[
a \ \Delta t \quad b \ \Delta t \quad c \ \Delta t \quad d \ \Delta t
\]
Where: $\Delta$ denotes change, $t$ time, and the square brackets molar concentration.

Since it is customary to define rates as positive quantities and the change in the concentration of the reactants is negative, the values $\Delta[A]$ and $\Delta[B]$ are preceded by minus sign so that the final result will be positive.

The units of rate are usually Ms$^{-1} = \text{mol L}^{-1} \text{s}^{-1}$ since concentrations are usually expressed in molarities and time in seconds. Occasionally other units such as mol s$^{-1}$ are used.

Most laboratory reactions that we come across or that you are likely to encounter ‘fast’ need only a few seconds or minutes to complete. The interval required for a chemical change or reaction to occur is called the reaction time. Every reaction has a reaction time and this varies from one reaction to another.

Since time is required for a given amount of substance to react, the reaction therefore has a rate. Reaction rates are not usually constant over a given reaction time. Strictly speaking the rate of a chemical reaction is a more definite and quantitative measurement that is determined by experiment. That is precisely why we have two kinds of rate expressions: the average and instantaneous rates. The average rate of a reaction is the average change in the concentration of a reactant or product per unit time over a given time interval while the instantaneous rate of a reaction is the rate of the reaction at a particular time.

The following sub–unit focuses on the factors that affect reaction rates and the way they influence reaction rate.

Molecules taking part in a chemical reaction do always need to overcome a certain minimum energy in order to undergo a chemical reaction and form products. This energy is called activation energy ($E_a$).

Because the energy of a substance is not uniformly distributed among its molecules, some may carry enough energy to react while others do not. For a chemical reaction to have noticeable rate, there should be noticeable number of molecules with the energy equal or greater than the activation energy. If the activation energy of a reaction is low, a greater proportion of the molecules involved in a reaction will have the minimum energy required to undergo reaction and the reaction will be fast.

A common analogy is pushing a boulder over a hill. The reactants are on one side like the boulder. The energy needed to push the boulder to the crest of the hill is like the activation energy. The products are like the condition when the boulder is at the bottom of the far side of the hill.
Fig 1.2. The sparks generated by striking steel against a flint provide the activation energy to initiate combustion in this Bunsen burner. The blue flame will sustain itself after the sparks are extinguished because the continued combustion of the flame is now energetically favorable. (http://www.answers.com/topic/activation-energy)

Reactant molecules with the energy equal or greater than the activation energy undergo chemical reaction and they may form an intermediate product whose chemical energy is higher than the combined chemical energy of the reactants known as the activated complex. Once the intermediate product, or activated complex, is formed, the final products are formed from it. The combined chemical energy of the final products may be less than that of the reactants when the reaction is exothermic and greater than that of the reactants when the reaction is endothermic. These conditions are illustrated by the energy diagrams given below.

The illustration in Fig. 1.3 shows the activation energy marked with a red arrow. It is the difference between the energy of the activated complex at the top of the hill and the energy of reactants.

**Activation energy**

The energy diagram in Fig. 1.4 illustrates the energy profile for an exothermic reaction. The vertical green arrow marks the heat of reaction. This is the difference in energy between the products and the reactants. In the energy diagram for an exothermic reaction, energy of the final products lies below that of the reactants on the x-axis.

**Energy**

The energy diagram in Fig. 1.5 illustrates the energy profile for an endothermic reaction. The vertical dark red arrow marks the heat of reaction. For an endothermic reaction, energy of the products lies above that of the reactants on the x-axis.

**Activation energy**

At the beginning of this unit it was pointed out that various reactions or changes that occur in nature or otherwise take place at a variety of speeds depending on the conditions. Why do these times for different changes turn out as they do? As the speed of an athlete depends on several factors such as temperature surroundings, wind direction, health condition etc. so is the speed of a chemical reaction affected by several factors. In general, the rate at which a given chemical reaction takes place depends upon a number of factors. The rates of chemical reactions can be affected by:

Reactant concentrations: Raising the concentration of reactants makes the reaction to happen at a faster rate.
In section 1.2 you have studied that for a chemical reaction to have noticeable rate, there should be noticeable number of molecules with the energy equal or greater than the activation energy. With an increase in concentration the number of molecules with the minimum required energy for a reaction to take place will increase and thereby the rate of the reaction increases. Suppose that at any one time 1 in a million particles have enough energy to equal or exceed the activation energy. If you had 100 million particles, 100 of them would react. If you had 200 million particles in the same volume, 200 of them would now react. The rate of reaction has doubled by doubling the concentration.

**Example: Zinc and hydrochloric acid**

In the lab, zinc granules react fairly slowly with dilute hydrochloric acid, but much faster if the acid is concentrated.

\[
\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2(\text{aq}) + \text{H}_2(\text{g})
\]

(2) Surface area: In reactions between solids and liquids, the surface area of the solid will affect how fast the reaction goes. This is because the two types of molecule can only bump into each other at the liquid solid interface, i.e. on the surface of the solid. So the larger the surface area of the solid, the faster the reaction will be.

Smaller particles have a bigger surface area than larger particle for the same mass of solid. The following example will enable you visualize this concept easily.

Consider the 6 x 6 x 2 brick shown above. The area of the surface facing the reader and its opposite is \(2(6 \times 6) = 72\) cm\(^2\). The remaining four surfaces will have an area of \(4(2 \times 6) = 48\) cm\(^2\). Thus, the area of the exposed surfaces of the brick is \(48 + 72 = 120\) cm\(^2\).

When the brick is dismantled into nine smaller cubes as indicated in fig.1.1. Each cube has a surface area of \(6(2 \times 2) = 24\) cm\(^2\). And, the total surface area of the nine cubes is \(9 \times 24 = 216\) cm\(^2\). This example clearly shows that the exposed surface area of a larger body will increase when it is divided into smaller pieces. Then, if a reaction takes place on the surface of a substance, increasing the surface area should increase the quantity of substance available to react and thus in turn will increase the rate of reaction. There is a simple way to visualize this. Take a loaf of bread and cut it into slices. Each time you cut a new slice, you get an extra surface onto which you can spread butter and jam. The thinner you cut the slices, the more slices you get and so the more butter and jam you can put on them. This is “Bread and Butter Theory”.

**Pressure**

Increasing the pressure on a reaction involving reacting gases increases the rate of reaction. Increasing the pressure of a gas is exactly the same as increasing its concentration. If you have a given mass of gas, the way you increase its pressure is to squeeze it into a smaller volume. If you have the same mass in a smaller volume, then its concentration is higher. Thus the effect is the same as the concentration effect.
Example: In the manufacture of ammonia by the Haber Process, the rate of reaction between the hydrogen and the nitrogen is increased by the use of very high pressures.

\[
\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{heat} \quad (\Delta H = -92 \text{ kJ mol}^{-1})
\]

In fact, the main reason for using high pressures is to improve the percentage of ammonia in the equilibrium mixture, but there is a useful effect on rate of reaction as well.

Changing the pressure on a reaction which involves only solids or liquids has no effect on the rate.

**Temperature**

It has been observed experimentally that a rise of 10°C in temperature usually doubles or triples the speed of a reaction between molecules.

The minimum energy needed for reaction, the activation energy, stays the same on increasing temperature. However, the average increase in particle kinetic energy caused by the absorbed heat means that a much greater proportion of the reactant molecules now has the minimum or activation energy to react. Thus, by increasing temperature, the energy levels of the molecules involved in the reaction will be raised and as a result the rate of the reaction increases.

It should be clear that if you can increase reaction rates by increasing temperature you can decrease reaction rates by lowering the temperature. You do this every time you put something in the refrigerator. To see the effect of elevated temperatures on reaction rates you can leave some dairy product out of the refrigerator for a few days and compare its condition with the same age dairy product that was kept cold.

**Presence or absence of a catalyst**

Catalysts are substances which increase the speed of a reaction by lowering the activation energy needed for the reaction to take place. A catalyst is not destroyed or changed during a reaction, so it can be used again.

For example, at ordinary conditions H2 and O2 do not combine. But in the presence of a small quantity of platinum, which acts as a catalyst, they combine and the reaction occurs rapidly.

\[
2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}
\]

**Nature of reactants**

Substances differ markedly in the rates at which they undergo chemical change. For example, hydrogen and fluorine molecules react explosively, even at room temperature, producing hydrogen fluoride molecules:
H₂ + F₂ → 2HF (very fast at room temp.)

Under similar conditions, hydrogen and oxygen molecules react so slowly that no chemical change is apparent:

2H₂ + O₂ → 2H₂O (Very slow at room temp.)

The differences in reactivity between reactions may be attributed to the different structures of the atoms and molecules of the reacting materials (for instance whether the substances are in solution or in the solid state—include). If a reaction involves two species of molecules with atoms that are already joined by strong covalent bonds (for example quartz (SiO₂) and water (H₂O)) collisions between these molecules at ordinary temperatures may not provide enough energy to break these bonds unlike the collisions which take place between molecules whose atoms are joined by weak covalent bonds. Therefore, reactions between molecules whose atoms are bound by weak covalent bonds take place at a faster rate than reactions between molecules whose atoms are bound by strong covalent bonds. For example, when methane gas is mixed with chlorine gas and exposed to sunlight an explosive reaction takes place in which chlorinated methane products are produced along with hydrogen chloride.

CH₄ + Cl₂ + energy → CH₃Cl + CH₂Cl₂ + CHCl₃ + CCl₄ + HCl

**Exercises**

Hydrogen gas is used for fuel aboard the Space Shuttle and may be used in Earth-bound engines of the future:

2H₂(g) + O₂(g) → 2H₂O(g)

a). Express the rate of this reaction in terms of changes in [H₂], [O₂], and [H₂O] with time.

b). When [O₂] is decreasing at 0.23 mol/L.s, at what rate is [H₂O] increasing?

Would a wet piece of iron metal rust faster in air or pure oxygen? Explain (Hint: consider the effect of concentration on reaction rate)

**Answers to 1a & 1b**

a) Rate = -Δ[H₂] / 2 Δt = -Δ[O₂] / Δt = 1 Δ[H₂O] / 2 Δt

b) Calculating the rate of change of [H₂O]:

35
1 $\Delta[H_2O] = - \Delta[O_2] = -(-0.23 \text{ mol/L.s})$

$2 \Delta t$ $\Delta t$

$\Delta[H_2O] = 2 \times 0.23 \text{ mol/L.s} = 0.46 \text{ mol/L.s}$

$\Delta t$

The balanced equation indicates that the number of moles of H$_2$O produced is twice the number of moles of O$_2$ consumed in the reaction. Therefore, it makes sense for the numerical value of the rate of $[H_2O]$ increase to be twice that of $[O_2]$ decrease.

Iron exposed to moist air will react with oxygen to form iron oxide. This oxidation process is called rusting.

$$4\text{Fe(s)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$$

Oxygen is more concentrated in its pure form than mixed with other gases in air. And we know that, as concentration increases the rate of a reaction will also increase. Therefore, a wet piece of iron metal will rust faster in pure oxygen than in air.

In section 1.2 we discussed how the rate of a chemical reaction depends on several factors such as temperature, catalyst, surface area of reactants, presence or absence of a catalyst, nature of reactants and concentration. We have seen qualitatively that the rates of most chemical reactions increase when the concentrations of the reactants increase. In this section, you will explore the quantitative relationships between the rate of a reaction and the concentrations of the reactants.

**Now consider the general reaction**

$$a\text{A} + b\text{B} \rightarrow \text{products (occurring at a constant temperature)}... \text{(1.3)}$$

where $A$ and $B$ represent the reactant formulae and, $a$ and $b$ represent the stoichiometric coefficients. In this section, you will study reaction rates that are not affected by the concentrations of the products. Therefore, you do not need to use symbols for the products.

In general, the rate of a reaction is proportional to the concentration of each reactant raised to some power, where the power on a given reactant is called, the order of the reaction with respect to that reactant. The overall order of a reaction is the sum of all the exponents of the concentration terms in the rate equation.

The rate for the above reaction can be given as

$$\text{Rate} \propto [\text{A}]^m[\text{B}]^n \text{...........................................1.4}$$

where $m$ and $n$ are the rate law exponents and indicate the order of the reaction with respect to the corresponding reactants. The values of $m$ and $n$ for a given reaction must be determined experimentally and do not change with temperature.
This relationship given by equation 1.4 can be expressed in a general equation given below, called the rate law equation.

\[
\text{Rate} = k \ [A]^m \ [B]^n \\
\text{……….1.5}
\]

The rate law equation expresses the relationship between the concentrations of the reactants and the rate of the reaction. The letter \( k \) represents a proportionality constant called the rate constant and it indicates how fast or slow a reaction is proceeding. A small rate constant indicates a slow reaction and a large rate constant indicates a fast reaction. The value of \( k \) for a given reaction is temperature dependent and is constant under constant temperature and pressure conditions.

The exponents \( m \) and \( n \) do not necessarily correspond to the stoichiometric coefficients of their reactants. Usually the value of a rate law exponent is 1 or 2. But, seldom values of 0, 3; and even fractions can occur. If the exponent for a given reactant is 1, then the reaction is said to be first order with respect to that reactant. Similarly, if the exponent of a reactant is 2, the reaction is said to be second order in this reactant. For example, the rate law equation below represents a reaction that is first order in \( A \), second order in \( B \), and third order (1 + 2) overall.

\[
\text{Rate} = k[A]^1[B]^2
\]

For example, the reaction between nitric oxide and ozone

\[
\text{NO(g)} + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)
\]

is first order in nitric oxide and first order in ozone. The rate law equation for this reaction is:

\[
\text{Rate} = k[\text{NO}]^1[\text{O}_3]^1
\]

The overall order of the reaction is \( 1 + 1 = 2 \).

The order of a reaction with respect to its reactants can be determined by running a series of experiments each of which starts with a different set of reactant concentrations and the initial rate is obtained. The experiments are designed to change one reactant concentration while keeping the other constant. This method of determining order of a reaction is known as the initial rate method.

**Example**

For the reaction \( A + B \rightarrow \text{products} \), the following rate data were obtained in three separate experiments:
<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Initial Concentration(M)</th>
<th>Initial rate M min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

a). What is the order of the reaction with respect to A and B?

b). What is the rate constant, k?

**Solution**

a) The general rate expression for this reaction is \( \text{Rate} = k[A]^x[B]^y \) and the values of \( x \) and \( y \) must be determined from the above data.

The data obtained shows that the rate doubles in experiment number 2 than it was in experiment number 1 when the concentration of \( B \) is doubled keeping \( A \) constant. In such a condition, when the rate of a reaction doubles by doubling the concentration of a given reactant, order of the reaction with respect to that reactant is 1. In experiment number 3 the rate is found not to change, than it was in experiment number 2, when the concentration of \( A \) is doubled. This indicates that the rate does not depend on the concentration of \( A \). This means, order of the reaction with respect to \( A \) is zero.

The experimentally determined rate equation will then be

\[
\text{Rate} = k[A]^0[B] = k[B] \quad \text{and the overall order} = 1
\]

The order with respect to each reactant can also be determined by calculation as follows:

\[
\text{Rate}_1 = 2 \times 10^{-5} \text{ M min}^{-1} = k[2]^x[1]^y
\]

\[
\text{Rate}_2 = 4 \times 10^{-5} \text{ M min}^{-1} = k[2]^x[2]^y
\]

Taking the ratio of the two rates we have

\[
\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{2 \times 10^{-5} \text{ M min}^{-1}}{4 \times 10^{-5} \text{ M min}^{-1}} = \frac{1}{2} k[2]^x[1]^y = k[2]^x[2]^y
\]

\[\Rightarrow \frac{1}{2} = 1^y \quad \text{since} \ x = 0 \]

\[2 = 2^y \]
Learning Activities

⇒ \( \frac{1}{2} = (1/2)y \)

Taking the logarithm of both sides will give us

\[
\log \left( \frac{1}{2} \right) = y \log \left( \frac{1}{2} \right)
\]

⇒ \( y = \frac{\log \left( \frac{1}{2} \right)}{\log \left( \frac{1}{2} \right)} = 1 \)

The order of the reaction with respect to the reactant A can be calculated by taking the ratio of the rate expressions of experiment number 2 and 3.

\[
\text{Rate}_2 = 4 \times 10^{-5} \text{ M min}^{-1} = k[2]^x [2]^y
\]

\[
\text{Rate}_3 = 4 \times 10^{-5} \text{ M min}^{-1} = k[4]^x [2]^y
\]

⇒ \( 1 = \frac{2}{4}x \)

⇒ \( 1 = \frac{1}{2}x \) \( \Rightarrow x = \frac{\log 1}{\log \left( \frac{1}{2} \right)} = 0 \)

Thus, the experimentally determined rate equation is given by

\[
\text{Rate} = k[A]^x[B]^y = k[A]_o[B] = k[B]
\]

Once we get the order of the reaction the rate constant can be calculated by taking the data obtained in any of the three experiments.

Consider experiment number 1

\[
\text{Rate} = k[1.0]
\]

⇒ \( 2 \times 10^{-5} \text{ M min}^{-1} = k \times 1.0 \text{ M} \)

⇒ \( k = 2 \times 10^{-5} \text{ M min}^{-1} = 2 \times 10^{-5} \text{ min}^{-1} \)

\[
1.0 \text{ M}
\]

**Example**

For the reaction \( X + 2Y + 2Z \rightarrow \text{products} \), the following rate data were obtained:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [X]</th>
<th>Initial [Y]</th>
<th>Initial [Z]</th>
<th>Initial rate of disappearance of X</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 M</td>
<td>0.1 M</td>
<td>0.1 M</td>
<td>1.0 \times 10^{-6} M/min</td>
</tr>
<tr>
<td>2</td>
<td>0.3 M</td>
<td>0.3 M</td>
<td>0.1 M</td>
<td>3.0 \times 10^{-6} M/min</td>
</tr>
<tr>
<td>3</td>
<td>0.4 M</td>
<td>0.1 M</td>
<td>0.1 M</td>
<td>1.0 \times 10^{-6} M/min</td>
</tr>
</tbody>
</table>
What is the order of each reactant in the system?

What is the value of the rate constant?

What is the rate of disappearance of X in experiment 4?

**Solution**

In the first experiment the rate of the reaction was determined to be $1.0 \times 10^{-6}$ M/min when the concentrations of all reactants were kept at 0.1 M.

In the second experiment the rate was found to be tripled when the concentrations of X and Y were tripled and that of Z was kept constant. This indicates that the rate of the reaction depends on the concentration on either X or Y or on both of them.

In the third experiment, the rate remained the same as in experiment number 1 when the concentration of X was quadrupled and those of Y and Z were kept constant. This fact indicates that, the rate of the reaction does not depend on the concentration of X.

Therefore, \[ \text{Rate} \propto [X]_0 \]

Going back to experiment number 2, the rate was tripled when the concentrations of X and Y were each tripled. But we have decided that the rate does not depend on the concentration of X. Therefore, the rate was tripled when the concentration of Y was tripled.

Thus, \[ \text{Rate} \propto [Y]_1 \]

When we compare experiments 2 and 4, neglecting X; the concentration of Y is kept constant while that of Z is tripled. As a result the rate was found to increase by a factor of 9.

Thus, \[ \text{Rate} \propto [Z]_2 \quad \text{since} \quad 9 = 3^2 \]

\[ k \] can be evaluated from any one of the 4 data sets, once orders are known; e.g., expt. 1.

\[
\begin{align*}
\text{Rate} &= k [X]_0 [Y]_1 [Z]_2 \\
K &= \text{rate} = 1.0 \times 10^{-6} \text{M/min} = 1.0 \times 10^{-3} \text{M}^{-2}/\text{min} \\
&= \frac{[Y]_1 [Z]_2}{(0.1 \text{M})(0.1 \text{M})^2}
\end{align*}
\]

When \([Z] = 0.15, [Y] = 0.15, \text{and } [X] = 0.125\), from balanced equation,

\[
\begin{align*}
\text{Rate} &= k [Y]_1 [Z]_2 \\
&= 10^{-3} \text{M}^{-2}/\text{min} (0.15)(0.15)^2 = 3.4 \times 10^{-6} \text{M/min}
\end{align*}
\]
Learning Activities

Note to the student: Read the PDF file “59-MeasRxnRates” in the CD accompanying this module for further understanding of determining the order of a reaction. In this file you have a detailed description of methods of determining order of a reaction and the rate constant.

In 1798, the chemist Claude Berthollet made an observation that contributed to an important discovery. Upon analyzing water from the Natron Lakes (a series of salt water lakes carved from limestone) he found large quantities of common salt, NaCl, and soda ash, Na₂CO₃. The result surprised Berthollet because he “knew” that a reaction between Na₂CO₃ and CaCl₂ goes to completion, forming NaCl and a precipitate of CaCO₃ as products.

\[
\text{Na}_2\text{CO}_3 + \text{CaCl}_2 \rightarrow 2\text{NaCl} + \text{CaCO}_3 \quad \quad \quad 1.6
\]

Understanding this, Berthollet expected that large quantities of NaCl and Na₂CO₃ could not coexist in the presence of CaCO₃. Since the reaction goes to completion, adding a large quantity of CaCl₂ to a solution of Na₂CO₃ should produce NaCl and CaCO₃, leaving behind no unreacted Na₂CO₃. In fact, this result is what he observed in the laboratory. The evidence from Natron Lakes, where the coexistence of NaCl and Na₂CO₃ suggests that the reaction has not gone to completion, ran counter to Berthollet’s expectations. Berthollet’s important insight was recognizing that the chemistry occurring in the Natron Lakes is the reverse of what occurs in the laboratory.

\[
2\text{NaCl} + \text{CaCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CaCl}_2 \quad \quad \quad 1.7
\]

Using this insight Berthollet reasoned that the reaction is reversible, and that the relative amount of “reactants” and “products” determine the direction in which the reaction occurs, and the final composition of the reaction mixture.

Similar to the reaction between Na₂CO₃ and CaCl₂ there are a number of reactions which seem to stop before the completion of the reactants. This is due to the fact that another reaction, the reverse of the first one, will start taking place as the concentrations of the products increase with time. Such reactions are known as reversible reactions. Reversible reactions are chemical reaction that may proceed in both the forward and reverse directions. In other words, the reactants and products of one reaction may reverse roles, without adding chemicals. They are represented by writing the equation either with arrows aimed in opposite directions as in the general equation given below, or with an equality sign in place of the arrows.

At the start of the reaction the forward reaction occurs rapidly; and with time, the concentrations of A and B go on decreasing. Due to this the rate of the forward reaction simultaneously decreases. On the other hand, the concentrations of C and D increase with time and as a result the rate of the reverse reaction (which initially was zero) increases.

Eventually the rates of the forward and reverse reactions become equal. At that time the reaction appears to stop, since there is no change in the concentration of all species involved in the reaction. At this point we say the reaction has reached a stage of chemical equilibrium.
More precisely the equilibrium is termed as dynamic equilibrium since reaction is still going on in the system but it seems that it has stopped since there is no net change in the concentration of reactants or products.

Chemical equilibrium is defined as the condition at which the forward and reverse reactions of a reversible reaction are taking place at the same rate, so there is no net change in the amounts of reactants or products.

Note that, it is the forward and the reverse reaction rates which will be equal at equilibrium. The concentrations of reactants and products at equilibrium may or may not be equal depending on the value of the equilibrium constant.

At equilibrium the forward reaction rate (Rf) of a reversible reaction will be equal to its reverse reaction rate (Rr).

According to the law of mass action expression, the rate of a chemical reaction is proportional to the product of the concentrations of the reactants each raised to a power equal to its coefficient in the balanced equation.

For the general reaction given in equation 1.8, rates of the forward reaction, Rfwd, and the reverse reaction, Rrev, are given by:

\[ R_{fwd} = K_f[A]^a[B]^b \] \[ \text{…………………1.9} \]

and \[ R_{rev} = K_r[C]^c[D]^d \] \[ \text{…………………1.10} \]

At equilibrium, the forward and the reverse reaction rates will be equal and we have,

\[ K_f[A]^a[B]^b = K_r[C]^c[D]^d \] \[ \text{…………………1.11} \]

or \[ \frac{K_f}{K_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \] \[ \text{…………………1.12} \]

But, \( \frac{K_f}{K_r} \) is a constant and is known as the equilibrium constant (Ke)

\[ \text{Therefore,} \quad K_e = \frac{[C]^c[D]^d}{[A]^a[B]^b} \] \[ \text{…………………1.13} \]

The law of chemical equilibrium states that, at any given temperature a chemical system reaches a state in which a particular ratio of reactant and product concentration terms has a constant value. Equation 1.13 is the mathematical expression for the law of chemical equilibrium.
By convention, the equilibrium concentrations of the substances appearing on the right hand side of the chemical equation (the products) are always placed in the numerator of the equilibrium constant expression and the concentrations of the substances appearing on the left hand side of the chemical equation (the reactants) are placed in the denominator.

For example, the equilibrium equation for the reaction between Na2CO3 and CaCl2

\[
\text{Na}_2\text{CO}_3 + \text{CaCl}_2 \rightleftharpoons 2\text{NaCl} + \text{CaCO}_3
\]

is given as

\[
K_e = \frac{[\text{NaCl}]^2[\text{CaCO}_3]}{[\text{Na}_2\text{CO}_3][\text{CaCl}_2]} \tag{1.15}
\]

The larger the value for the equilibrium constant the more the reaction goes to completion. Irreversible reactions can be thought to have an infinite equilibrium constant so there are no reactants left.

**What does Ke tell?**

The number values for equilibrium constants are tied to the nature of reactants and products in a reaction. The number values for Ke are gotten from experiments measuring equilibrium concentrations. The number value tells the equilibrium ratio of products to reactants. In an equilibrium mixture both reactants and products coexist.

- The value for Ke is large when products dominate the mixture.
- The value for Ke is small when the reactants dominate the mixture.
- The expression for an equilibrium reaction is determined by the coefficients in the balanced equation.
- Large Ke > 1 ⇒ products are “favored”
- Ke = 1 ⇒ neither reactants nor products are favored
- Small Ke < 1 ⇒ reactants are “favored”

The term “favored” means that side of the equation has higher numbers of moles and higher concentrations than the other.

Large Ke have values that are huge, 1 x 1034

Ke = 1 neither reactants nor products are favored

Small Ke have values that are tiny, 4 x 10-41
A heterogeneous equilibria is an equilibria in which more than a single phase appears in the reaction. For example, equilibrium between solid and gas, liquid and gas, solid and liquid, solid and solid, immiscible liquids are all heterogeneous equilibria.

For example, the following equilibrium system involves both gaseous and solid phases:

\[ \text{C(s)} + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g) \] \hspace{1cm} \text{1.16}

The equilibrium expression for this reaction could be written as,

\[ K'\text{e} = \frac{[\text{CO}]^2}{[\text{C}]\text{[CO}_2]} \] \hspace{1cm} \text{1.17}

However, the concentration of a pure solid and liquid per unit volume is always the same since these substances are characterized by a density that is the same for all samples regardless of their size. Therefore, the concentration of carbon in the above equilibrium is a constant; and the equilibrium constant can be written as,

\[ K'\text{e} = \frac{[\text{CO}]^2}{\text{K}[\text{CO}_2]} \] \hspace{1cm} \text{1.18}

\[ (K'\text{e})\text{[K]} = K\text{e} = \frac{[\text{CO}]^2}{[\text{CO}_2]} \] \hspace{1cm} \text{1.19}

Thus, in heterogeneous reactions, the substances included in the equilibrium constant expression are those which are present in the homogeneous phase.

**Calculations involving chemical equilibrium!**

In chemical equilibrium calculations (a) if the value of Ke is known for a given reaction, it can be calculated for any related reaction or (b) if all concentrations are known at equilibrium the Ke can be calculated, or if the Ke is known and the initial concentrations are given, the equilibrium concentration can be calculated. Consider the following examples. Example 1.3

Calculate the equilibrium concentrations of H\(_2\), I\(_2\) and HI if 0.200 mole of each of H\(_2\) and I\(_2\) are placed in a 1.00L flask at 425\(^\circ\)C. (Ke = 54.5)

**Solution.**

The chemical equation for the reaction is, \( \text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI} \), for which the equilibrium constant expression is given by,

\[ \text{Ke} = [\text{HI}]^2 \]
At the beginning of the reaction, 
\[ [\text{H}_2] = [\text{I}] = 0.200 \text{ mol/L and } [\text{HI}] = 0 \]

Let the quantity of H2 reacted at equilibrium be x mol/L.

Then, at equilibrium, 
\[ [\text{H}_2] = [\text{I}_2] = (0.200-x) \text{ mol/L and } [\text{HI}] = 2x \text{ mol/L} \]

Now substitute the equilibrium concentrations in the equilibrium constant equation and solve for x.

\[
\begin{align*}
\text{Ke} &= \frac{(2x)^2}{(0.200-x)^2} \\
2x &= (54.5)^{\frac{1}{2}} = \pm 7.38
\end{align*}
\]

We have to choose the positive square root since there is no negative concentration.

\[ 2x = 7.38 (0.200-x) \Rightarrow 2x = 1.476 - 7.38x \Rightarrow 9.38x = 1.476 \]

\[ x = \frac{1.476}{9.38} = 0.157 \]

Thus, at equilibrium, 
\[ [\text{HI}] = 2x = 2 \times 0.157 = 0.314 \text{ mol/L} \]

and, 
\[ [\text{H}_2] = [\text{I}_2] = 0.200 - 0.157 = 0.043 \text{ mole/L} \]

Example 1.4 For the reaction in example given above, calculate Ke if the initial concentrations of each of H2 and I2 is 0.400mol/L and at equilibrium the amount of each left unreacted is 0.086 mol/L.

**Solution.**

If 0.086mol/L of each of H2 and I2 are left in the reaction, then the quantity of each which has reacted will be, 
\[ 0.400 - 0.086 = 0.314 \text{mol/L} \]

From the balanced equation we see that when one mole of each of H2 and I2 react, the quantity of HI produced is 2 moles. Therefore, if 0.314 mol/L of each of H2 and I2 have reacted at equilibrium, the quantity of HI produced will be 
\[ 2 \times 0.314 = 0.628 \text{ mol/L} \]

Now substitute the above equilibrium concentrations in the equilibrium constant equations and solve for Ke.
\[
\text{Ke} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.628)^2}{(0.086)^2} = 53.3
\]

In most cases the effect of a change in environmental conditions upon a chemical equilibrium can be predicted with the aid of Le Chatelier's Principle. Le Chatelier's Principle states that when a stress is applied to a chemical equilibrium, the equilibrium changes in a way which minimizes the effect of the stress. Accordingly, the following factors are found to cause a shift in equilibrium.

**Concentration**

As the concentration (or partial pressure of a gas) of any of the reactants or products of a chemical reaction at equilibrium changes, the equilibrium shifts in such a way as to overcome that change – that is to relieve the stress put on the system (according to Le Chatelier's principle) and to keep Keq constant (that is the concentration of the other products and reactants change in such a way that the value of the Keq remains constant). Generally, if the concentration of one of the reactants is increased, the reaction occurs to form more products. If the concentration of one of the products is increased, the reverse reaction occurs to form more reactants. If the concentration of one or more of the products of the reaction is decreased, the reaction occurs in a way which will partially replenish the decreased concentration.

**Example**

When a solution containing red iron thiocyanate complex is divided into three parts and one of these is treated with excess iron (III), and the other with excess thiocyanate. The color gets darker in each case.

\[
\text{Fe}^3+(aq) + \text{SCN}-(aq) \rightleftharpoons \text{FeSCN}_2^+(aq) \quad \text{.................1.20}
\]

The color of FeSCN\(_2^+\) complex is brick red. The fact that the color of the solution gets darker upon the addition of excess iron (III) and excess thiocyanate indicates that the equilibrium shown by the equation 1.20 shifts to the right.

**Temperature**

Temperature changes can affect a chemical equilibrium whenever heat is absorbed (an endothermic reaction) or emitted (an exothermic reaction) during the reaction.

Consider the following two reactions:

a) \(3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3 + \text{heat}\)  

b) \(\text{CaCO}_3 + \text{heat} \rightleftharpoons \text{CaO} + \text{CO}_2\)
If a reaction is exothermic, as reaction (a) above, an increase in temperature results in an increase in the equilibrium concentration of the reactants and a decrease in the equilibrium concentration of the products, i.e., a shift in the equilibrium to the left.

In an endothermic reaction (i.e. if we treat heat as though it were a chemical reagent, then a rise in temperature “adds” heat to the system and a drop in temperature “removes” heat from the system. As with a change in any other parameter (concentration, pressure or volume) the system shifts to reduce or counteract the effect of the change) a temperature increase favours the endothermic direction (from left to right of the equilibrium equation; and a temperature decrease favours the exothermic reaction.

In an endothermic reaction of the type shown by equation (b), when temperature of the system is increased, the direction of the reaction which can use some of the heat is the forward direction. Therefore, an increase in temperature results in an increase in the concentration of the products and a decrease in concentration of the reactants; while a decrease in temperature causes an increase in the concentrations of the reactants and a decrease in the concentrations of the products.

Note that an increase in the temperature of an exothermic reaction in the forward direction decreases the Ke value. And for a reaction that is endothermic in the forward direction, Ke increases with increasing temperature. If a reaction neither emits nor absorbs heat, temperature has no effect upon equilibrium concentrations, and thus on the Ke.

In addition to affecting the value of the equilibrium constant, temperature also affects the rate of a chemical reaction, i.e., the time necessary for the reaction to reach equilibrium. The rate of many chemical reactions approximately doubles for every 10oC increase in temperature.

**Pressure**

Pressure change can have a major effect upon the position of the chemical equilibrium if one or more of the participants in the chemical reaction are gases. But it has no marked effect on the position of equilibrium in reactions where all the reactants and products are either solids or liquids, because these phases are hardly compressible.

Increasing the pressure of a gas is exactly the same as increasing its concentration. If you have a given mass of gas, the way you increase its pressure is to squeeze it into a smaller volume. If you have the same mass in a smaller volume, then its concentration is higher.

You can also show this relationship mathematically by the ideal gas equation, which you have learned in your General Chemistry I module.

**Rearranging this gives:**

Because “RT” is constant as long as the temperature is constant, this shows that the pressure is directly proportional to the concentration. If you double one, you will also double the other.
Therefore, an increase in pressure (decrease in volume) favours the net reaction that decreases the total number of moles of gases and a decrease in pressure (increase in volume) favours the net reaction that increases the total number of moles of gases.

Consider the reaction for the formation of NH₃,

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) -92\text{kJmol}^{-1} \]

The total number of moles of reactants is four and that of products is two. When the reaction proceeds from left to right, the total number of moles of the gases will decrease and vice-versa.

When the pressure of the equilibrium is increased the concentration of the gases will also increase. The equilibrium then shifts to the right so that the total number of moles of the gases (and thus the concentration) will decrease. Therefore, increasing the pressure of the reaction between N₂ and H₂ will favour the production of more NH₃.

In general, increasing the pressure of a mixture of gases that are at equilibrium shifts the equilibrium in the direction which forms the fewest number of molecules of gas.

When there are the same number of molecules of gaseous reactants and products on both sides of the equation as in the reaction between N₂ and O₂ to produce NO, given below,

\[ \text{N}_2(g) + \text{O}_2 \rightleftharpoons 2\text{NO}(g) \]

Pressure changes will not influence the amounts of the various substances present in the reaction mixture at equilibrium. This is because there is no way for the system to counteract pressure changes placed on it.

If the pressure of a mixture of gases at equilibrium is increased by introducing an inert (a non-reacting) gas, it will not affect the position of the equilibrium because it will not alter the partial pressures or the concentrations of any of the substances already present.

**Catalyst**

A catalyst is used to decrease the time required to reach chemical equilibrium without altering the value of the equilibrium constant for the reaction.

**Example**

Indicate how each of the following changes affect the amount of H₂ and Ke in the system below, for which \( \Delta H \) reaction = + 41kJ

\[ \text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g) \]
Learning Activities

a) Addition of CO₂ b) Addition of H₂O c) Addition of a catalyst
d) Increase in temperature e) Decrease in the volume of the container

Solution

a). For a reaction at equilibrium, increasing the concentration of any of the reactants of the forward reaction forces the reaction to proceed in the forward direction. Therefore, addition of CO₂ decreases the amount of H₂ in the system.

The Ke expression for the given reaction is,  \[ Ke = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} \]

Since concentration of the products increase when the equilibrium shifts to the right Ke will increase.

b). Addition of H₂O means increasing the concentration of a reactant for the reverse reaction, and this favors the reverse reaction to proceed, and increases the amount of H₂.

Ke decreases due to the decrease in the concentration of the products and the increase in the concentration of the reactants

c). Addition of a catalyst may hasten the velocity of the reaction. It neither affects the equilibrium concentration of H₂ nor the value of Ke.

d). \( \Delta H_{\text{reaction}} = \Delta H_{\text{formation of products}} - \Delta H_{\text{formation of reactants}} \).

Therefore, \( \Delta H_{\text{reaction}} = +ve \) implies that, \( \Delta H_{\text{formation of products}} \) is greater than \( \Delta H_{\text{formation of reactants}} \) and the reaction is endothermic.

In an endothermic reaction an increase in temperature favors the formation of products. Thus the concentration of H₂ decreases and Ke increases when the temperature of the equilibrium reaction is increased.

e). A decrease in the volume of the container causes an increase in pressure (concentration). Since both the right and left hand side reactions produce the same number of moles of gaseous products there is no way that the equilibrium will minimize pressure by decreasing concentration. Therefore, there will be no effect on the amount of H₂ and Ke when the pressure of the equilibrium is increased by decreasing the volume of the container.
Formative Assessment

1. Write the rate law equation for the reaction: \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \)

2. Describe the factors that affect reaction rate and discuss how each factor is affecting rate.

3. A series of experiments were carried out for the reaction between oxygen and nitric oxide, \( \text{O}_2(g) + 2\text{NO}(g) \rightarrow 2\text{NO}_2(g) \), and the initial rate of the reactions were determined. The data obtained is given below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [O2]</th>
<th>Initial [NO]</th>
<th>Initial Rate (M s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.10 \times 10^{-2}</td>
<td>1.30 \times 10^{-2}</td>
<td>3.21 \times 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>2.20 \times 10^{-2}</td>
<td>1.30 \times 10^{-2}</td>
<td>6.40 \times 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>1.10 \times 10^{-2}</td>
<td>2.60 \times 10^{-2}</td>
<td>12.8 \times 10^{-3}</td>
</tr>
<tr>
<td>4</td>
<td>3.30 \times 10^{-2}</td>
<td>1.30 \times 10^{-2}</td>
<td>9.60 \times 10^{-3}</td>
</tr>
<tr>
<td>5</td>
<td>1.10 \times 10^{-2}</td>
<td>3.90 \times 10^{-2}</td>
<td>28.8 \times 10^{-3}</td>
</tr>
</tbody>
</table>

a) What is the order of each reactant in the system?

b) What is the value of the rate constant?

4. Define the Le chatelier’s principle.

5. What do you understand by the term dynamic equilibrium? Write down equilibrium constant expression for the following reaction:

\[
2\text{NH}_3 (g) \rightleftharpoons 3\text{H}_2(g) + \text{N}_2(g)
\]

In what direction will the chemical equilibrium shift if pressure is increased?

6. In what direction will the chemical equilibrium of the following reversible reactions shift when a) temperature is decreased b) pressure is decreased?

i) \( \text{2SO}_2 + \text{O}_2 \rightleftharpoons \text{2SO}_3 + 192.74 \text{kJ} \)

ii) \( \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 - 54.47\text{kJ} \)

7. Calculate the equilibrium constant, \( K_e \), for the reaction, \( 2\text{HBr } \rightleftharpoons \text{H}_2 + \text{Br}_2 \), if the initial mass of hydrogen bromide is 0.809g and 5% of it has reacted by the moment when the chemical equilibrium was attained.
8. The reaction, $\text{CH}_4 + \text{H}_2\text{O(vapour)} \rightleftharpoons \text{CO} + 3\text{H}_2$, occurs in a 500mL flask. Calculate the equilibrium constant for this system if the initial masses of the reactants are: CH4 0.8g, H2O 0.9g, CO 1.4g, H2 0.1g; and by the time chemical equilibrium has been attained, 50% of methane has already reacted.

9. How may the position of equilibrium be shifted?

10. At a certain temperature, the composition of a system at equilibrium in a volume of 10L is the following: CO 11.2g; Cl2 14.2g; and COCl2 19.8g. Calculate the equilibrium constant of the reaction CO + Cl2 $\rightleftharpoons$ COCl2 under the given conditions.

11. At a certain temperature, 21.2 moles of hydrogen and 5.23 moles of iodine were mixed in a closed vessel. Determine the composition of this mixture at equilibrium, if the equilibrium constant of the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ is 50.

12. What effect would decreasing the volume of the reaction mixture have on the equilibrium condition in each of the following reactions?
   
   a) $\text{C(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2(g)$
   
   b) $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
   
   c) $4\text{HCl(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{Cl}_2\text{(g)} + 2\text{H}_2\text{O(g)}$

13. The exothermic reaction, $\text{A(g)} + \text{B(g)} \rightleftharpoons 2\text{C(g)}$, proceeds to an equilibrium condition at a temperature of 200°C. Which of the following statements is/are true? Explain.
   
   a). If the mixture is transferred to a reaction vessel of twice the volume, the amounts of reactants and products will remain unchanged.
   
   b). Addition of a catalyst will result in the formation of a greater amount of C(g).
   
   c). Lowering the reaction temperature to 100°C will not alter the equilibrium condition.
   
   d). Addition of an inert gas, such as helium, will have little or no effect on the equilibrium.

14. If the equilibrium constant of a reaction at equilibrium is found to decrease when the equilibrium temperature is changed, is the forward reaction endothermic or exothermic? Explain.

**Identify the true or false statement**

In a reaction at equilibrium, the number of moles of products formed will be equal to the number of moles of reactants undergone reaction.
In a reaction at equilibrium, the number of moles of reactants reacted will be equal to the number of moles of reactants left unreacted.

The position of equilibrium will be affected more significantly by a change in temperature than a change in pressure if the reactants and products are solids or liquids.

If the forward reaction of an equilibrium is exothermic, its equilibrium constant (Ke) will decrease if the temperature of the system is increased.

In a chemical equilibrium where all reactants and products are gases, an increase in P or in T will shift the direction of the reaction in the forward direction if the forward reaction is endothermic and the total number of moles of reactants is greater than the total number of products.

Multiple Choice questions

In a reversible reaction at equilibrium,

the total number of moles of the products is greater than the total number of moles of the reactants left unreacted the total number of moles of products is equal to the total number of moles of reactants left unreacted.

The total number of moles of products is equal to the total number of moles of reactants consumed in the reaction.

The number of moles of substances formed in the forward direction in a unit time is equal to the number of moles of substances formed in the reverse direction.

Which of the following is correct about the equilibrium, \( xA(g) + yB(g) \rightleftharpoons mC(g) + nD(g) \), if the forward reaction is exothermic?

An increase in temperature and pressure will shift the equilibrium in the forward direction if \( x + y \) is less than \( m + n \).

An increase in temperature will shift the equilibrium in the reverse direction and an increase in pressure in the forward direction if \( x + y \) is less than \( m + n \).

An increase in temperature or pressure will shift the reaction in the reverse direction if \( x + y \) is less than \( m + n \).

An increase in pressure or temperature will have no influence if \( x + y = m + n \).

Which of the following is not an example of the Le-Chatelier's principle?
If the concentration of any one of the reactants of the reverse direction are increased, the position of an equilibrium shifts in the reverse direction.

In a mixture of gases in the same container if the concentration of one of the gases is increased, its partial pressure will also increase.

In a reaction at equilibrium, increasing temperature will shift the equilibrium to the endothermic direction.

Increasing the pressure of an equilibrium where all reactants and products are gases will shift the equilibrium to the direction where the total number of moles is smaller.

Which of the following increases $K_e$?

- Increasing the concentration of the reactants of the forward direction without changing the temperature.
- Increasing the temperature of an equilibrium where the forward direction is exothermic.
- Increasing the temperature of an equilibrium where the reverse direction is exothermic.

Increasing the pressure of an equilibrium of gaseous reactants and products where the number of moles of products is greater than the number of moles of reactants.

**Learning activity # 2**

Title of Learning Activity: Solutions and their Properties

**Specific Teaching and Learning Objectives:**

At the end of this learning activity you should be able to:
- Describe the various types of solutions
- Define the various types of concentration units
- Calculate the concentrations of solutions by using different concentration units
- Define solubility and describe how temperature affects solubility
- Describe colligative properties

Summary of the learning activity:

In the course ‘General Chemistry I’ we discussed the properties associated with the three states of matter. For the most part, however, these discussions applied to pure substances. But it is only rarely that we encounter pure materials, either in our daily activities or in the laboratory. Usually, the chemicals with which we work occur in mixtures, and very often these are solutions. When two or more substances homogeneously mix to form a mixture, one will have a marked effect on the properties of the other. Many times, the effects observed can provide us with useful information about the way substances interact with one another.

In this unit we will discuss the various types of solutions and take a close look at how solutions are formed to explore the changes that occur when one substance dissolves in another. We will also describe the various concentration units used for quantifying solutions since it would be meaningless to talk about solutions without knowing how to express the quantity of substance dissolved in a given volume of another substance. Furthermore we shall discuss some basic concepts on solubility, and colligative properties of solutions. Solved examples and exercises are provided at the end of sub-units. Most of these examples and exercises are intended to help you develop conceptual and quantitative problem solving skills. At the end of the unit, there are exercises that you will be required to work through, on completing your various readings.

List of relevant readings

- Solutions in http://chemmovies.unl.edu/ChemAnime/index.htm
**List of relevant resources:**

- Computer with internet facility to access links and relevant copy-write free resources.
- CD-Rom accompanying this module for compulsory readings and demonstrations.
- Multimedia resources like video, VCD and CD players.

**List of relevant useful links:**


2. Understanding Chemistry, by Jim Clark

**In VIRTUAL CHEMBOOK,**

at http://www.elmhurst.edu/~chm/vchembook/index.html

1. Solution and Solubility, by Elmhurst College, by Charles E.Ophardt, c. 2003, a review on solutions, the solution process are discussed in depth.

**Detailed description of the activity:**

In nature, very few pure substances are found and solutions are so common.
Most chemical reactions that are carried out in the laboratory and in industry, and that occur in living organisms, take place not between pure solids, liquids or gases, but in solution, among ions and molecules dissolved in water or other solvents. Solutions allow intimate and varied encounters between molecules of different kinds, a condition that is essential for rapid chemical reactions to occur. Therefore, solutions are extremely important in chemistry and it is worth devoting a significant amount of time to the subject of solutions.

What are solutions?

Solutions are defined as homogeneous mixtures of the molecules, atoms or ions of two or more substances. The components of a solution are frequently referred to as solute and solvent. A solute is generally taken as the substance which dissolves and a solvent is a fluid phase that dissolves a solid, liquid, or gaseous solute resulting in a solution. Thus for gas-liquid and solid-liquid solutions the former is the solute and the latter is the solvent. When both the components of a solution are liquids and are present in different proportions, the major component is considered to be the solvent and the minor component the solute. However, for solutions where the two liquid components of a solution are present in equal proportions, one is justified to call each as either the solvent or solute.

From cytoplasm to tree sap, gasoline to cleaning fluid, iced tea to urine, solutions in which a liquid is the solvent appear throughout everyday life. Therefore, we usually think of a solution as a homogeneous mixture of a gas, liquid, or solid solute in a liquid solvent (i.e., gas-liquid, liquid-liquid, or solid-liquid solutions).

However, solutions can also exist as gases, where different kinds of gases mix homogeneously (gas-gas solutions), and solids, where molten metals mix homogeneously as in most natural minerals and many alloys (solid-solid solutions).

From everyday experience you know that some compounds such as alcohol dissolve in water at any proportion while others such as carbon tetrachloride do not dissolve. What factors limit the mutual solubilities of substances? Experience has shown that substances with similar types of intermolecular forces dissolve in each other. This fact is summarized in the old rule-of-thumb like dissolves like, which usually provides a good qualitative means of predicting solubility.

In-order to understand the factors that limit the mutual solubilities of substances, let us picture a general solute and solvent about to form a solution and see the steps taking place when the solute dissolves in the solvent.

Science conceptually breaks down the solution process into the following three steps.

1. The solute is placed in the solvent and the solute particles slowly separate from each other.
2. The molecules of the solvent begin to move out of the way and they make room for the molecules of the solute.
3. The solute and solvent interact with each other (solvent-solute interaction) until the solute is uniformly distributed throughout the solvent. In a sense, the solute particles in the solution occupy positions that are normally taken by solvent molecules.

Therefore, whether a given solute dissolves in a certain solvent or not depends on the relative forces of attraction of solvent molecules for each other, solute particles for each other, and the strength of the solute-solvent interactions. If the strength of the attractive forces between pairs of solvent molecules and between pairs of solute molecules are of nearly the same magnitude solvent and solute molecules can replace each other and as a result solubilization takes place. However, if the attractive force between solute and solvent molecules is weaker than the force between pairs of solvent or solute molecules solubilization does not take place. Now let us see the situation by considering the various types of solutions separately.

The energy associated with the mixing of two gases is negligible and all gases are infinitely soluble in one another. Air is a common example of a gaseous solution, consisting of about 18 gases in widely differing proportions. There are many gaseous solutions which are used by human being by controlling the proportions of the components. For example, anesthetic gas proportions are finely adjusted to the needs of the patient and the length of the surgical procedure. The ratios of components in many industrial gas mixtures, such as CO:H2 in syngas (a fuel mixture of CO and H2) production or N2:H2 in ammonia production, are controlled to optimize product yield under varying conditions of temperature and pressure.

Unlike gaseous solutions, each gas has only a limited solubility in a given liquid. Gases that are non-polar, such as N2, or nearly so, such as NO, have low boiling points because their intermolecular attractions are weak. Likewise, they are not very soluble in water because solute-solvent forces are weak. Table 2.1 shows, for non-polar gases, boiling point generally correlates with solubility in water.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Solubility (M) (at STP)</th>
<th>bp (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4.2 x 10^-4</td>
<td>4.2</td>
</tr>
<tr>
<td>Ne</td>
<td>6.6 x 10^-4</td>
<td>27.1</td>
</tr>
<tr>
<td>N2</td>
<td>10.4 x 10^-4</td>
<td>77.4</td>
</tr>
<tr>
<td>CO</td>
<td>15.6 x 10^-4</td>
<td>81.6</td>
</tr>
<tr>
<td>O2</td>
<td>21.8 x 10^-4</td>
<td>90.2</td>
</tr>
<tr>
<td>NO</td>
<td>32.7 x 10^-4</td>
<td>121.4</td>
</tr>
</tbody>
</table>

In some cases, the small amount of a non-polar gas that does dissolve is essential to a process. The most important environmental example is the solubility of O2 in water.
At 25°C and 1 atm, only 3.2 mL O₂ dissolves per 100 mL water, but aquatic animal life would die without the presence of this small amount.

The greatest solubilities of gases occur when they react chemically with the solvent or another component. Oxygen for example seems much more soluble in blood than in water because the O₂ is continually bonding with hemoglobin molecules in red blood cells. Similarly, carbon dioxide, which is essential for aquatic plants growth, seems very soluble in water (about 81 mL/100 mL at 25°C and 1 atm) because it is actually reacting, in addition to simply dissolving:

\[
\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq}) \]

Liquids unlike gases do not form solutions in any proportions. Each liquid has only a limited solubility in the other, and once either of these limits is exceeded, the mixture separates into two phases.

Consider the situation between benzene and carbon tetrachloride and, water and carbon tetrachloride. Benzene (C₆H₆) dissolves in carbon tetrachloride (CCl₄) but not in water. Both benzene and carbon tetrachloride are non-polar compounds and experience only relatively weak London forces. The strength of the attractive forces between pairs of benzene molecules and between pairs of carbon tetrachloride molecules are of nearly the same magnitude as between molecules of benzene and carbon tetrachloride. By comparison, the strength of the attractive forces between water and the non-polar carbon tetrachloride molecules is much weaker. Thus, when the two compounds are mixed, water molecules tend to stick together simply because they attract each other much more strongly than they do with molecules of carbon tetrachloride.

Ethanol and water, where both species are polar and exhibit hydrogen bonding are mixed a solution is formed. The attractive forces between pairs of water molecules and between pairs of ethanol molecules have a nearly same magnitude as the strength of the attractive force between molecules of water and ethanol.

Ionic solids are insoluble in most non-aqueous solvents. However, many of them are soluble in water because the strong bond between the ions of the salts and the polar water molecules are very similar to the strong attractions between the ions themselves and, therefore, substitute for them. Consider the dissolution of NaCl to clearly visualize the dissolution of salts. Initially, the positive (Na⁺) and the negative (Cl⁻) ions are only attracted to each other. The water molecules are held together by a strong hydrogen bond (See Fig. 2.1). If the crystal is to dissolve, these bonds must be broken.

During dissolution negative chloride ions on the surface are attracted by neighboring positive sodium ions and by the partially positive hydrogen atom in the polar water molecule (See Fig.2.2). Similarly, the positive sodium ions are attracted by both chloride ions and the partially negative oxygen atom in the polar water molecule. A “tug-of-war” occurs for the positive and negative ions between the other ions in the crystal and the water molecules. Several water molecules are attracted to each of the ions.
Whether the crystal dissolves, is determined by which attractive force is stronger. If the internal ionic forces in the crystal are the strongest, the crystal does not dissolve. If the attractions for the ions by the polar water molecules are the strongest, the crystal will dissolve. This is the situation in sodium chloride.

Once the ions are released from the crystals, the ions are completely surrounded by water molecules. Note that the proper atom in the water molecule must “point” toward the correct ion. The charge principle and the partial charges in the polar molecule determine the correct orientation. Partially negative oxygen atoms in the water molecule interact with the positive sodium ion and partially positive hydrogen atoms in the water molecule interact with the negative chloride ion. Heat of solution is closely related to the possible formation of a solution. Each of the three steps of solution formation listed in section 2.1 either require external energy to take place or release energy. Heat of solution (ΔH) is then defined as the quantity of energy that is absorbed or released when a solution is formed. It is the difference between the energy possessed by the solution after it has been formed and the energy that the components of the solution had before they were mixed;

\[ \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{soln}} \]

The first step in the formation of a solution is separation of solute particles from each other. Then, solvent particles separate to make room for the solute particles.

These steps require energy input to break attractive intermolecular forces; therefore they are endothermic. No matter what the nature of the attractions within solute and solvent, some energy is absorbed when particles of the solute or solvent separate in the above two steps. Thus, the processes in the two steps are endothermic (i.e., \( \Delta H_{\text{solute}} \) and \( \Delta H_{\text{solvent}} > 0 \)). On the other hand, when solute and solvent molecules mix and attract each other (step 3) energy is released. This process is exothermic (\( \Delta H_{\text{soln}} < 0 \)).

Dissolution overall can be either endothermic or exothermic, depending on whether more energy was used to break the bonds, or more energy was released when new bonds were formed.

If more energy is released in making bonds than is used in breaking bonds (\( \Delta H_{\text{soln}} < \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} \)), the overall process is exothermic and \( \Delta H_{\text{soln}} \) is negative. If more energy is used than is released (\( \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} > \Delta H_{\text{soln}} \)), the overall process is endothermic and \( \Delta H_{\text{soln}} \) is positive. The more positive the value of \( \Delta H_{\text{soln}} \), the less soluble is the solute in that solvent and the more negative its value is the more soluble is the solute.

**Exercise**

The heat of solution for AlCl3 is \(-321 \text{ kJ mol}^{-1}\). Calculate the total heat liberated by dissolving 10.0 g of AlCl3 in 1.00 L of water.

Ans. 24.1 kJ

In gas-liquid or solid-liquid solutions, there is a certain maximum limit of solute that can be dissolved in a given volume of the solvent at a given temperature and pressure.
The maximum amount of the compound, which can dissolve in a specific volume of a solute at a specific temperature and pressure, is known as its solubility. A solution that has dissolved the maximum quantity of solute that it can dissolve at that particular temperature is said to be a saturated solution. However, if the solution contains less than this quantity it is said to be an unsaturated solution. There are also solutions that contain more quantity of solute than the quantity which they can dissolve under a saturated state. For instance, when a saturated solution of sodium acetate is cooled slowly and carefully, the excess sodium acetate will not crystallize out as the temperature decrease. Thus, the solution contains more solute than it can dissolve at the lower temperature. Such solutions are said to be supersaturated solutions. Supersaturated solutions are unstable. Once the supersaturated solution has been prepared, addition of a very small amount of solute will cause the excess solute to crystallize out of the solution immediately.

Solubility is often expressed in grams of solute per liter or per 100 cm³ or 100 g of solvent at specified temperature. Other units such as mol/liter are also used.

Liquids which are mutually miscible (for example ethanol and water) mix in all proportions. The same is true for gaseous mixtures or solid mixtures. These solutions can not be saturated and the term solubility has no meaning for such solutions. Several factors affect the solubility of a compound either by altering the value of the solubility product or by shifting the equilibrium in a manner which changes the solubility.

Temperature has a major effect on the solubility of most substances. You may have noticed, for example, that not only does sugar dissolve more quickly in hot tea than in iced tea, but more sugar dissolves: the solubility of sugar is greater at higher temperature. Generally in most, but not all, cases the solubility of a solid substance increases with temperature. The key to this effect of temperature is the equilibrium nature of solubility.

As you saw in unit 1, when a system at equilibrium is disturbed, it adjusts itself to reestablish equilibrium. Consider a saturated solution that has a positive heat of solution. Since heat is absorbed to form the solution, we can think of the heat as if it were a reactant:

\[
\text{Solute} + \text{solvent} + \text{heat} \rightleftharpoons \text{saturated solution}
\]

If the temperature of the system is raised (more heat added), the system absorbs some of the added heat by increasing the rate of the forward process. More solute dissolves and equilibrium becomes reestablished with more ions in solution. Generally, solubility increases with temperature if the solution process is endothermic.

If a solute has a negative heat of solution, heat is given off:

\[
\text{Solute} + \text{solvent} \rightleftharpoons \text{saturated solution} + \text{heat}
\]

In the same way, when the temperature of this system is raised, the system will absorb some heat in response to a heat rise. In this case, however, it does so by increasing the rate of the reverse process. Some solute crystallizes out and equilibrium becomes reestablished with fewer ions in solution. Generally, solubility decreases with temperature if the solution process is exothermic. In the case gas-liquid solutions, the gaseous particles start out far apart as a pure solute.
Therefore, for a gas, $\Delta H_{\text{solute}} \approx 0$. Since the process which involves interaction between gaseous molecules and water molecules is exothermic ($\Delta H_{\text{soln}} < 0$), the sum of these two terms must be negative. Thus, in the dissolution of a gas in water the overall process is exothermic.

$$\text{Solute(g)} + \text{water(l)} \rightleftharpoons \text{saturated solution (aq)} + \text{heat}$$

The above equation means that gas solubility in water decreases with rising temperature.

**Example**

From the following information, predict whether the solubility of each compound increases or decreases with an increase in temperature:

a) $\Delta H_{\text{soln}}$ of NaOH(s) = -44.5 kJ/mol.

b) When KNO3 dissolves in water, the solution becomes cold.

c) CsCl(s) $\rightleftharpoons$ Cs+(aq) + Cl-(aq); $\Delta H_{\text{soln}} = +17.8$ kJ

**Solution**

a) A negative $\Delta H$ means the process is exothermic, so when 1 mol NaOH dissolves in water, 44.5 kJ of heat is released:

$$\text{NaOH (s)} \rightleftharpoons \text{Na+(aq)} + \text{OH-(aq)} + \text{heat}.$$  

A higher temperature (more heat) decreases the solubility of NaOH.

b) During solubilization a solution becomes cold when heat is absorbed (the solution process is endothermic).

$$\text{KNO3(s)} + \text{heat} \rightleftharpoons \text{K+(aq)} + \text{NO3-(aq)}$$

Therefore, a higher temperature increases the solubility of KNO3.

c) The positive $\Delta H$ means heat is absorbed when CsCl dissolves:

$$\text{CsCl(s)} + \text{heat} \rightleftharpoons \text{Cs+(aq)} + \text{Cl-(aq)}$$

A higher temperature increases the solubility of CsCl.

**Exercise**

Predict whether the solubility increases or decreases at lower temperature and give the sign of $\Delta H_{\text{soln}}$ for the following cases:

a) When sodium cyanate (NaOCN) dissolves, the solution becomes hot.
b) $\text{KF(s)} \rightleftharpoons \text{K}^+(\text{aq}) + \text{F}^-(\text{aq}) + 17.7 \text{ kJ}$

Since liquids and solids are almost incompressible, pressure has little effect on their solubility. In contrast, it has a major effect on gas solubility. Consider the piston – cylinder assembly in Figure 2.4, with a gas above a saturated aqueous solution of the gas. At a given pressure, the same number of gas molecules enter and leave the solution per unit time; that is, the system is at equilibrium:

$$\text{Gas} + \text{solvent} \rightleftharpoons \text{saturated solution}$$

If the piston is pushed down, the gas volume decreases, its pressure increases, and gas particles collide with the liquid surface more often. Therefore, more gas particles enter than leave the solution per unit time. Higher gas pressure disturbs the balance at equilibrium, so more gas dissolves to reduce this disturbance (the above equation shifts to the right) until the system reestablishes equilibrium.

(A) A saturated solution of a gas is in equilibrium at pressure $P_1$. (B) If the pressure is increased to $P_2$, the volume of the gas decreases. As a result, the frequency of collisions with the surface increases and more gas is in solution when equilibrium is reestablished. Henry's law expresses the quantitative relationship between gas pressure and solubility: the solubility of a gas ($S_{\text{gas}}$) is directly proportional to the partial pressure of the gas ($P_{\text{gas}}$) above the solution:

$$S_{\text{gas}} = k_H \times P_{\text{gas}} \quad \text{…………………………………2.3}$$

where $k_H$ is the Henry’s law constant and is specific for each gas-solvent combination at a given temperature. With $S_{\text{gas}}$ in mol/L and $P_{\text{gas}}$ in atm, the units of $k_H$ are mol/L . atm.

**Example**

At 25°C oxygen gas collected over water at a total pressure of 101 kPa is soluble to the extent of 0.0393 g/L. What would the partial pressure of oxygen collected in the same way be if its solubility was determined to be 0.043 g/L.

**Solution**

The total pressure, 101 kPa, is the sum of the partial pressures of water vapour and oxygen. The partial pressure of water at 25°C = 3.17 kPa.

Thus, partial pressure of oxygen ($P_{O2}$) = $P_{\text{total}} - PH_{2O}$

$$P_{O2} = (101 - 3.17)kPa = 97.83 \text{ kPa}$$

Henry's law = $S_{\text{gas}} = k_H \times P_{\text{gas}} \Rightarrow S_{\text{gas}} / P_{\text{gas}} = k_H$
This means that, the ratio of the concentration (solubility) of a gas to its partial pressure is a constant. Then, for a given gas at two different conditions of pressure,

\[
\frac{(S_{\text{gas}})_{1}}{(P_{\text{gas}})_{1}} = \frac{(S_{\text{gas}})_{2}}{(P_{\text{gas}})_{2}}
\]

\[
(S_{\text{O}_2})_{1} = 0.0393 \text{ g/L}; \quad (S_{\text{O}_2})_{2} = 0.043 \text{ g/L};
\]

\[
(P_{\text{O}_2})_{1} = 97.83 \text{ kPa}; \quad (P_{\text{O}_2})_{2} = \text{?}
\]

\[
(P_{\text{O}_2})_{2} = \frac{(S_{\text{O}_2})_{2} \times (P_{\text{O}_2})_{1}}{(S_{\text{O}_2})_{1}} = \frac{0.043 \text{ g/L} \times 97.83 \text{ kPa}}{0.0393 \text{ g/L}}
\]

\[
(P_{\text{O}_2})_{2} = 107.04 \text{ kPa}
\]

**Exercise**

The partial pressure of ethane over a saturated solution containing \(6.56 \times 10^{-2}\) g of ethane is 100.1 kPa. What is its partial pressure when the saturated solution contains \(5.0 \times 10^{-2}\) g of ethane?

Ans. 76.3 kPa

There are several reasons why we need to learn concentration units. Quantitative study of a solution requires knowing its concentration, that is, the amount of solute present in a given amount of solution. Chemists use several different concentration units, each of which has advantages and disadvantages.

Knowledge of concentration units is also necessary when working with equilibrium problems, a major topic in general chemistry. You must know concentration units to solve problems involving osmotic pressure, boiling point elevation, and freezing point depression.

Let us examine the most common or frequently used units of concentration: mass percent, mole-fraction, molarity, and molality.

Note: Many students have a problem of understanding concentration units because 1) they don’t clearly understand the mole concept 2) they have trouble grasping concentration material is their lifelong use of memorized formulae to obtain numerical answers. Therefore, you should be familiar with the mole concept and try to solve concentration related problems using intuition, logic, definition and dimensional analysis.

Percent by mass is defined as the ratio of the mass of a solute to the mass of the solution multiplied by 100 percent.

Before applying percent by mass to chemical problems let us consider the following problem.
Assume your weight is 100 kg and 30 kg of your total weight is fat. What percent by weight is the fat in your body?

You probably figured out, almost intuitively, that 30% of your body weight is fat. This is determined by dividing the weight of the fat by the total body weight and multiplying by 100.

\[
\text{i.e., } \% \text{ by mass fat} = \frac{\text{mass of fat}}{\text{total body mass}} \times 100 \% \]

\[
= \frac{30}{100} \times 100 \% = 30\%
\]

In chemical application, the percent by mass is defined as

\[
\text{Percent by mass (w/w \%) } = \frac{\text{Msolute}}{\text{Msolute + Msolvent}} \times 100\% \]

\[
\frac{\text{Msolute}}{\text{Msolution}} \times 100\% \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad 2.4
\]

The percent by mass has no units because it is a ratio of two similar quantities.

In commerce, medicine, and other applied fields of Chemistry, (w/w) measures is often used, and is commonly expressed as weight-percent concentration, or simply “percent concentration”. For example, a solution containing 5 g of NaCl in 95 g of H2O is a 5% solution of NaCl.

**Exercise**

A solution is made up of three different substances: 20 g of ethanol, 29 g of water, and 1 g of sodium chloride. What is the percent by weight of the alcohol?

Ans. 40% by weight of alcohol.

Mole Fraction is defined as the moles of one component divided by Total Moles of Components in solution.

You also know the basic ideas associated with mole fraction. Consider a class made up of 25 girls and 75 boys. What fraction of the class is female?

**The female fraction of the class is 25/100 or 0.25.**

The mole fraction concept is very similar to the female fraction concept. The mole fraction of a component of a solution, say, component A, is written XA and is defined as

\[
XA = \frac{\text{moles of A}}{\text{Total Moles of Components}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad 2.5
\]
Sum of moles of all components

The mole fraction has no units, since it too is a ratio of two similar quantities.

**Example**

The mole fraction of a solution which is prepared by adding 200.4 g of pure ethanol (C₂H₅OH) to 143.9 g of water will be

\[
X_{\text{C₂H₅OH}} = \frac{200.4 \text{ g}}{46.02 \text{ g mol}^{-1} \text{C₂H₅OH}} + \frac{143.9 \text{ g}}{18.02 \text{ g mol}^{-1} \text{H₂O}} = 0.353
\]

**Exercise**

A solution is made up of 10 mol of water, 1.0 mol of sodium hydroxide, and 2.0 mol of sugar. What is the mole fraction of the sodium hydroxide?

Ans. 0.077

Molarity is a concentration unit which tells us the number of moles of solute that are dissolved in 1.0 L of a solution.

Molarity is defined as the number of moles of solute in a liter of solution; that is,

\[
M = \frac{\text{Number of moles of solute}}{\text{Volume of solution in L}} \quad \text{2.6}
\]

For example, the molar concentration of a solution in which 49 g of H₂SO₄ is dissolved in 500 mL of solution will be,

\[
M_{\text{H₂SO₄}} = \frac{49 \text{ g}}{98 \text{ g mol}^{-1} \text{H₂SO₄}} = 1 \text{ M}
\]

**Exercise**

If 80 g of sodium hydroxide is present in 500 mL of solution, what is the molarity of the sodium hydroxide in this solution? Ans. 4.0 M

The molality of a species in solution is the number of moles of that solute per kilogram of solvent.

\[
\text{Molality (m)} = \frac{\text{moles of solute}}{\text{mass of solvent in kg}} \quad \text{2.7}
\]
For example, the molal concentration of a solution in which 49 g of H2SO4 is dissolved in 750 g of water will be,

\[
m_{\text{H2SO4}} = \frac{49 \text{ g}}{98 \text{ g mol}^{-1} \text{ H2SO4}} = 0.67 \text{ m}
\]

\[
750 \text{ g} / 1000 \text{ g kg}^{-1}
\]

**Exercise**

A solution of sodium hydroxide is prepared by mixing 1 mol of NaOH with 500 g of water. Find the molality of this solution. Ans. 2 m

The four concentration terms have various uses. For instance, the mole fraction unit is not generally used to express the concentration of solutions for titration and gravimetric analysis, but it is useful for calculating partial pressures of gases and for dealing with vapor pressures of solutions.

Molarity has an advantage in that it is generally easier to measure the volume of a solution, using precisely calibrated volumetric flasks, than to weigh the solvent. For this reason, molarity is often preferred over molality. On the other hand, molality is independent of temperature, since the concentration is expressed in number of moles of solute and mass of solvent, whereas the volume of a solution generally increases with increasing temperature. A solution that is 1.0 M at 25°C may become 0.97 M at 45°C because of the increase in volume. This concentration dependence on temperature can significantly affect the accuracy of an experiment.

Percent by mass is similar to molality in that it too is independent of temperature since it is defined in terms of ratio of mass of solute to mass of solution. Furthermore, we do not need to know the molar mass of the solute in order to calculate the percent by mass.

The above ways of expressing concentration are inter-convertible when the density of the solution is known.

**Example**

Suppose a 0.396 molal glucose (C6H12O6) solution is prepared. Express the concentration of this solution in molarity and mass percent.

**Solution**

The mass of the solution must be converted to volume in working problems of this type. The density of the solution is used as a conversion factor. Since a 0.396 m glucose solution contains 0.396 mole of glucose in 1 kg of water, the total mass of the solution is


(0.396 mol C₆H₁₂O₆ x 180.2 g) + 1000 g H₂O solution = 1071 g

1 mol C₆H₁₂O₆

From the known density of the solution (1.16 g/mL), we can calculate the molarity as follows:

\[ M = \frac{0.396 \text{ mol C}_6\text{H}_12\text{O}_6 \times 1.16 \text{ g soln} \times 1000 \text{ mL soln}}{1071 \text{ g soln \times 1 mL soln}} = 0.429 \text{ mol C}_6\text{H}_12\text{O}_6 = 0.429 \text{ M} \]

\[ \frac{1 \text{ L soln}}{1 \text{ L soln}} \]

Although you will deal with colligative properties of solutions in depth in your physical chemistry course, it is worth to be introduced to these important properties of solutions at this stage.

Solutions have different properties than either the solutes or the solvent used to make the solution. Those properties can be divided into two main groups—colligative and non-colligative properties. Colligative properties of solutions are those properties which depend only on the number of dissolved particles in solution and not on their identity. Non-colligative properties depend on the identity of the dissolved species and the solvent.

To explain the difference between the two sets of solution properties, we will compare the properties of a 1.0 M aqueous sugar solution to a 0.5 M solution of table salt (NaCl) in water.

Despite the concentration of sodium chloride being half of the sucrose concentration, both solutions have precisely the same number of dissolved particles because each sodium chloride unit creates two particles upon dissolution—a sodium ion, Na⁺, and a chloride ion, Cl⁻. Therefore, any difference in the properties of those two solutions is due to a non-colligative property. Both solutions have the same freezing point, boiling point, vapor pressure, and osmotic pressure because those colligative properties of a solution only depend on the number of dissolved particles. The taste of the two solutions, however, is markedly different. The sugar solution is sweet and the salt solution tastes salty. Therefore, the taste of the solution is not a colligative property. Another non-colligative property is the color of a solution. A 0.5 M solution of CuSO₄ is bright blue in contrast to the colorless salt and sugar solutions. Other non-colligative properties include viscosity, surface tension, and solubility.

Vapour pressure lowering, boiling point elevation and freezing point depression!

When a nonvolatile solute is dissolved in water, the vapour pressure of the solution is always less than that of pure water. Due to this vapour pressure lowering the boiling-point of water will increase (boiling point elevation) and its freezing point will decrease (freezing point depression).
The freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure are all related to one another, because the magnitude of the change depends on the concentration of solute particles. It is also dependent on the nature of the solvent. These properties are not so much dependent on the nature of, or the chemical properties of the solute that is dissolved, but simply on the number of solute particles present, whether they are ions or molecules doesn’t make too much difference except in the number. It is the concentration that make the difference, not the nature. Of course, that concentration does have to take into account whether that solute dissociates and if so, how much. Because of this they are all grouped together as a set of properties, and they are called the colligative properties.

1. Define the terms, solution, solute, solvent and solubility.

2. What is meant by a saturated, unsaturated and super-saturated solution?

3. Express the concentration of a solution made by dissolving 10g of 100% H2SO4 in 90g of water and which has a density of 1.4g/cm3 in
   a) weight percent
   b) molarity
   c) normality
   d) molality.

4. The Henry’s law constant for a gas dissolved in water was found to be 4.88 x 10^{-4} g L^{-1} kPa^{-1} at 250C. In an experiment the gas was collected over water and its concentration was found to be 0.0478 g L^{-1}. What was the total pressure of gas above the solution if the vapour pressure of water at 250C is 3.17 kPa?

5. How does the solubility of a gas and a solid in a liquid change with an increase in temperature?

6. How many grams of each of the following salts is needed to prepare 2.5 L of 2 M solution?
   A) KCl   b) KOH   c) (NH4)2CO3   d) Al2(SO4)3

7. What kind of properties of solutions are described to be colligative properties? Give examples.

8. If a solution is prepared with hot water having a temperature of 500C and its concentration is expressed in one of the following concentration units its value will not change when the temperature of the solution decreases to 250C. This concentration unit is,
   a) Molarity       b) molality     c) normality     d) %(w/v)

When 1.0 M solution of NaCl is diluted

the number of moles of NaCl in the solution remains the same

the number of moles of NaCl per unit volume decreases

the molar concentration of NaCl remains the same.
The concentration of NaCl remains the same but the number of moles of NaCl per unit volume decreases.

Among the factors which influence solubility, a solid-liquid solution is least affected by a change in

- a) temperature
- b) pressure
- c) type of solvent
- d) pH of the solution

When a non-volatile non-electrolyte solute is dissolved in a liquid solvent,

- a) the vapor pressure and boiling point of the liquid increases while its freezing point is decreasing.
- b) the vapor pressure of the liquid decreases while its boiling point and freezing increase
- c) the vapor pressure and freezing of the liquid decrease while its boiling increases
- d) the vapor pressure, boiling point and freezing point of the liquid increase

**Learning activity # 3**

**Title of Learning Activity: Energy and Chemical Reactions**

**Specific Teaching and Learning Objectives:**

At the end of this learning activity you should be able to:

- State and explain the law of conservation of energy
- Draw energy profiles of exothermic and endothermic reactions
- Do stoichiometric calculations in thermochemical reactions

**Summary of the learning activity:**

When substances undergo chemical reactions and form products, there is always an accompanying change in the energies of the reactants. Therefore, it would be useful to consider the energy changes that accompany chemical reactions.

In this unit we will discuss the first law of thermodynamics and the concepts associated with energy exchange between bodies in a system. Most chemical reactions either absorb or release energy during the reaction process. The key concepts underlying the release or absorption of energy during a chemical reaction are also described in relation to the rate of reaction.
Solved examples and exercises are provided mainly in the subunit dealing with the stoichiometry of thermochemical reactions. Most of the examples and exercises will help you develop conceptual and quantitative problem solving skills on issues discussed in the unit. Finally, there are exercises that you will be required to work through on completing your various readings at the end of the unit.

List of relevant readings:


List of relevant resources:

- Computer with Internet facility to access links and relevant copy-write free resources.
- CD-Rom accompanying this module for compulsory readings and demonstrations.
- Multimedia resources like video, VCD and CD players.

List of relevant useful links:

In the links given below you will find discussions and tests with answers on energy and chemical reactions.


Detailed description of the activity:

Most physical changes, chemical reactions, and nuclear reactions are accompanied by changes in energy. The energy changes are crucial to life on Earth. For example, chemical reactions in your body generate the heat that helps to regulate your body temperature. Physical changes, such as evaporation, help to keep your body cool. On a larger scale, there would be no life on Earth without the energy from the nuclear reactions that take place in the Sun.
The study of energy and energy transfer is known as thermodynamics. Chemists are interested in the branch of thermodynamics known as thermochemistry: the study of energy involved in chemical reactions. There are a number of terms and definitions in which thermochemists agreed in order to discuss energy and its interconversions. You will learn about these terms and definitions over the next few pages and then you will examine the energy changes that accompany reactions.

All changes in matter, whether chemical or physical, are accompanied by changes in the energy content of the matter. When wood is burned and converted to ash and gases, its energy content decreases, and that change in energy is released as heat and light. Energy is absorbed when snow melts and is released when water vapor condenses to rain. The chemical energy of a gasoline is converted to mechanical energy when it is used as a fuel in cars. Many such transfer of energy exist in our universe. But what happens to the overall energy of our universe? Will it gradually decrease? Increase? Or remain constant? Following, we shall discuss the fundamental law of energy and the concepts underlying this law.

We have seen that, when wood burns it loses energy and the energy lost is gained by the surrounding. When a snow melts the heat from the surrounding is gained by the snow. The chemical energy in gasoline is converted to mechanical energy. Energy in general can be converted from one form to another as it is transferred from one body to another. It cannot simply appear or disappear.

This idea is generalized by the fundamental law of energy called the law of conservation of energy. The law of conservation of energy states that the total energy of the universe is constant. In other words, this means that, energy can be neither destroyed nor created but transferred from one substance to another. This idea can be expressed by the following equation:

\[ \Delta E_{\text{universe}} = 0 \]

To have a meaningful discussion on energy let us first define the terms system and surrounding.

System: is defined as the part of the universe that is being studied and observed. In a chemical reaction, the system is usually made up of the reactants and products. By contrast, the surroundings are everything else in the universe. The relationship between the universe, a system, and the system’s surroundings can be expressed by the following two equations.

\[ \text{Universe} = \text{System} + \text{Surroundings.} \]

\[ \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} \]

These relationships tell us that, any change in the system is accompanied by an equal and opposite change in the surroundings.

\[ \Delta E_{\text{system}} = - \Delta E_{\text{surroundings}} \]
We often represent this change with an energy diagram in which the final and initial states are horizontal lines on a vertical energy axis (Fig. 3.1). The change in internal energy, $\Delta E$, is the difference between the heights of the two lines.

**Example**

The heat released from gasoline burning in a car engine caused the products CO2 and H2O to expand and push 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 energy.

**Solution**

The system in this case is the reactants and products of the reaction. The surroundings are the pistons, the cooling system, and the rest of the car. Heat is released by the system, so $q$ is negative. $\Delta E$ is the sum of the heat used up to push the pistons and the heat lost to heat the surrounding.

Thus, $\Delta E = -325 \text{ J} + (-451 \text{ J}) = -776 \text{ J}$.

Most physical and chemical changes, including those that take place in living systems, occur in the constant-pressure conditions of our atmosphere. In the laboratory, for example, reactions are generally carried out in beakers, flasks, or test tubes that remain open to their surroundings and hence to a pressure of approximately one atmosphere (1 atm). To express the heat released or absorbed in a constant-pressure process, chemists use a quantity called enthalpy, represented by the symbol $H$.

The change in enthalpy of a system during a process at constant pressure, represented by $\Delta H$, is equal to the heat given off or absorbed by the system during the process. The enthalpy of reaction is the difference between the enthalpies of the products and the enthalpies of the reactants:

$$\Delta H = H(\text{products}) - H(\text{reactants}) \quad \text{..................3.4}$$

Enthalpy of reaction can be positive or negative, depending on the process. For an endothermic process (heat absorbed by the system from the surroundings), $\Delta H$ is positive. For an exothermic process (heat released by the system to the surroundings), $\Delta H$ is negative.

Now let us apply the idea of enthalpy changes to two common processes: (1) the combustion of hydrogen gas in oxygen is one of many familiar chemical reactions that release considerable quantities of energy and it is an exothermic reaction.

$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{energy}$$
On the other hand, the decomposition of mercury(II) oxide (HgO) at high temperatures:

\[
\text{Energy} + 2\text{HgO(s)} \rightarrow 2\text{Hg(l)} + \text{O}_2(g)
\]

is an endothermic process.

The difference in the energies is the heat supplied by the system to the surroundings. Just the opposite happens in endothermic reactions. Here, the difference in the energies of the products and reactants is equal to the heat supplied to the system by the surroundings.

To appreciate the phenomenon of endothermic and exothermic reactions read the following description on the way how the bombardier beetle defends itself.

\[
a) \text{C}_6\text{H}_4\text{(OH)}_2(aq) + \text{H}_2\text{O}_2(aq) \rightarrow \text{C}_6\text{H}_4\text{O}_2(aq) + 2\text{H}_2\text{O}(l)
\]

To estimaet the heat of reaction, let is consider the following steps

\[
b) \text{C}_6\text{H}_4\text{(OH)}_2(aq) \rightarrow \text{C}_6\text{H}_4\text{O}_2(aq) + \text{H}_2(g) \quad \Delta\text{Ho} = 177 \text{ kJ}
\]
\[
c) \text{H}_2\text{O}_2(aq) \rightarrow \text{H}_2\text{O}(l) + \frac{1}{2} \text{O}_2(g) \quad \Delta\text{Ho} = -94.6 \text{ kJ}
\]
\[
d) \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta\text{Ho} = -286 \text{ kJ}
\]

The heat of reaction for (a) is simply the sum of those for (b), (c), and (d). Therefore, we write

\[
\Delta\text{Ho}_a = \Delta\text{Ho}_b + \Delta\text{Ho}_c + \Delta\text{Ho}_d
\]

\[
= (177 - 94.6 - 286) \text{ kJ} = -204 \text{ kJ}
\]

The large amount of heat generated is sufficient to heat the mixture to its boiling point. By rotating the tip of its abdomen, the beetle can quickly discharge the vapor in the form of a fine mist toward an unsuspecting predator. In addition to the thermal effect, the quinones also act as a repellent to other insects and animals. An average bombardier beetle carries enough reagents in its body to produce about 20 to 30 discharges in quick succession, each with an audible detonation.
Fig. 3.3 A bombardier beetle discharging a chemical spray.

The bombardier beetle has a pair of glands that open at the tip of its abdomen. Each gland consists basically of two compartments. The inner compartment contains an aqueous solution of hydroquinone and hydrogen peroxide, and the outer compartment contains a mixture of enzymes. When threatened, the beetle squeezes some fluid from the inner compartment into the outer compartment, where, in the presence of the enzymes, an exothermic reaction takes place:

In chemical reactions, enthalpy changes result from chemical bonds being broken and formed. Breaking a bond is a process that requires energy. Creating a bond is a process that releases energy. For example, consider the combustion reaction that takes place when nitrogen reacts with oxygen.

\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) \]

In this reaction, one mole of nitrogen-nitrogen triple bonds and one mole of oxygen-oxygen double bonds are broken. Two moles of nitrogen-oxygen bonds are formed. This reaction absorbs energy.

In other words, this means that more energy is released to form two nitrogen-oxygen bonds than is used to break one nitrogen-nitrogen bond and one oxygen-oxygen bond. This reaction is therefore, an endothermic reaction. In an exothermic reaction, more energy is released to form bonds than is used to break bonds.

The enthalpy change of a chemical reaction is known as the enthalpy of reaction, \( \Delta \text{H}_{\text{rxn}} \). The enthalpy of reaction is dependent on conditions such as temperature and pressure. Therefore, we often talk about the standard enthalpy of reaction, \( \Delta \text{H}_{\text{rxn}} \): the enthalpy change of a chemical reaction that occurs at STP (25°C and 100 kPa). Often, \( \Delta \text{H}_{\text{rxn}} \) is written simply as \( \Delta \text{H}_\circ \).

The simplest way to represent the enthalpy change of an exothermic reaction is to use a thermochemical equation: a balanced chemical equation that indicates the amount of heat that is absorbed or released by the reaction it represents. For example, consider the exothermic reaction of one mole of hydrogen gas with half a mole of oxygen gas to produce liquid water. For each mole of hydrogen gas that reacts, 285.8 kJ of heat is produced. Notice that the heat term is included with the products because heat is produced.

\[ \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) + 285.8 \text{kJ} \]

You can also indicate the enthalpy of reaction as a separate expression beside the chemical equation. For exothermic reactions, \( \Delta \text{H}_\circ \) is always negative.
H$_2$(g) + $\frac{1}{2}$ O$_2$(g) → H$_2$O(l) \hspace{1cm} \Delta H^o = -285.8 \text{ kJ}

A third way to represent the enthalpy of reaction is to use an enthalpy diagram. See the figure below how this is done.

The endothermic decomposition of solid magnesium carbonate produces solid magnesium oxide and carbon dioxide gas. For each mole of magnesium carbonate that decomposes, 117.3 kJ of energy is absorbed. As for an exothermic reaction, there are three different ways to represent the enthalpy change of an endothermic reaction.

The enthalpy of reaction can be included as a heat term in the chemical equation. Because heat is absorbed in an endothermic reaction, the heat term is included on the reactant side of the equation.

$117.3 \text{ kJ} + \text{MgCO}_3(s) \rightarrow \text{MgO}(s) + \text{CO}_2(g)$

The second and third ways of representations are given as follows:

MgCO$_3$(s) → MgO(s) + CO$_2$(g) \hspace{1cm} \Delta H^o = 117.3 \text{ kJ}

A good way to record the enthalpy change for a particular reaction is through a thermochemical equation, a balanced equation that also states the heat of reaction (\(\Delta H_{\text{rxn}}\)). One thing to always keep in mind is that the \(\Delta H_{\text{rxn}}\) value shown refers to the enthalpy change for the amounts of substances in that specific reaction.

The enthalpy change of any process has two aspects:

1. Sign. The sign of \(\Delta H\) depends on the direction of the change. The sign of a forward reaction is opposite that of the reverse reaction.

Decomposition of 2 mol of water to its elements (endothermic):

$2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \hspace{1cm} \Delta H_{\text{rxn}} = 572 \text{ kJ}$

Formation of 2 mol water from its elements (exothermic):

$2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) \hspace{1cm} \Delta H_{\text{rxn}} = -572 \text{ kJ}$

Magnitude. The magnitude of \(\Delta H\) is linearly dependent on the quantity of substance in the reaction. That is, if the amount of products formed doubles, the enthalpy change also doubles. Because of this relationship, an exothermic reaction that is relatively safe on a small scale may be extremely dangerous on a large scale.

For the formation of 2 mol water from its elements \(\Delta H = -572 \text{ kJ}\), while for the formation of 1 mol \(\Delta H = -286 \text{ kJ}\).
Example

Aluminium reacts readily with chlorine gas to produce aluminum chloride. The reaction is highly exothermic.

\[ 2\text{Al}(s) + 3\text{Cl}_2(g) \rightarrow 2\text{AlCl}_3(s) \quad \Delta H^\circ = -1408 \text{ kJ} \]

What is the enthalpy change when 1.0 kg of Al reacts completely with excess Cl2?

Solution

The atomic weight of aluminum is 26.98 g/mol

1.0 kg or 1000 g of Al is then, \( 1000 \text{ g} / 26.98 \text{ g mol}^{-1} = 37 \text{ mol} \)

From the given equation, we can see that, when 2 moles of Al react with Cl2 the enthalpy change (\( \Delta H^\circ_1 \)) is -1408 kJ. Then what is required is to calculate the enthalpy change (\( \Delta H^\circ_2 \)) when 37 mol of Al react.

\[
\begin{align*}
2 \text{ mol} &= -1408 \text{ kJ} \\
37 \text{ mol} &= \ ?
\end{align*}
\]

Use the ratio \( \Delta H^\circ_2 = n_2 \text{ mol Al} \)

\[
\begin{align*}
\Delta H^\circ_1 &= n_1 \text{ mol Al} \\
\Delta H^\circ_2 &= 37 \text{ mol} \times -1408 \text{ kJ} \\
&= -26048 \text{ kJ}
\end{align*}
\]

Formative evaluation:

1. If an athlete is feeling warm after exercising, has he increased the internal energy of his body? Explain.

2. State and explain the law of conservation of energy.

3. Classify the following processes as exothermic or endothermic:
   a) freezing of water; b) boiling of water; c) condensation of water vapour; d) digestion of food; e) a person running; f) a person growing; g) wood being chopped; h) heating with a furnace.
4. For which of the following reactions would you expect the percent dissociation to increase with increasing temperature? Explain.

   a) \( \text{NO}(g) \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \quad \Delta H = -21.57 \text{ kCal.} \)
   
   b) \( \text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \quad \Delta H = + 23.64 \text{ kCal} \)
   
   c) \( \text{N}_2\text{H}_4(g) \rightleftharpoons \text{N}_2(g) + 2\text{H}_2(g) \quad \Delta H = -22.80 \text{ kCal} \)
   
   d) \( \text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g) \quad \Delta H = +25.88 \text{ kCal} \)

5. The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be represented by

   \( \text{Al}_2\text{O}_3(s) \rightarrow 2\text{Al}(s) + \frac{3}{2} \text{O}_2(g) \quad \Delta H_{\text{rxn}} = 1676 \text{ kJ} \)

   If aluminum is produced this way, how many grams of aluminum can form when 1.0 x 103 kJ of heat is transferred?

6. Draw an enthalpy diagram for a general a) exothermic b) endothermic reaction; label axis, reactants, products, and \( \Delta H \) with its sign.

7. Write a balanced equation and draw an approximate enthalpy diagram for each of the following changes: a) the combustion of 1 mol liquid ethanol (\( \text{C}_2\text{H}_5\text{OH} \)); b) the formation of 1 mol nitrogen dioxide from its elements (heat is absorbed).

8. Would you expect \( \text{O}_2(g) \rightarrow 2\text{O}(g) \) to have a positive or a negative \( \Delta H_{\text{rxn}} \)? Explain.

9. Is \( \Delta H \) positive or negative when 1 mol water vapour condenses to liquid water? Why? How does this value compare with the value from the vaporization of 2 mol liquid water to water vapour?

10. When 1 mol KBr(s) decomposes to its elements, 394 kJ of heat is absorbed.
    
    a) Write a balanced thermochemical equation equation for this reaction.
    
    b) How much heat is released when 10.0 kg KBr forms from its elements?

11. A mercury mirror forms inside a test tube by the thermal decomposition of mercury (II) oxide:

    \( \text{2HgO(s)} \rightarrow 2\text{Hg(l)} + \text{O}_2(g) \quad \Delta H_{\text{rxn}} = 181.6 \text{ kJ} \)

    a) How much heat is needed to decompose 555 g of the oxide?

    b) If 275 kJ of heat is absorbed, how many grams of mercury form?

12. Sucrose (\( \text{C}_{12}\text{H}_{22}\text{O}_{11} \)), is oxidized in the body by \( \text{O}_2 \) via a complex set of reactions that ultimately produces \( \text{CO}_2(g) \) and \( \text{H}_2\text{O}(g) \) and releases 5.64 x 103 kJ/mol heat.
a) Write a balanced thermochemical equation for this reaction.

b) How much heat is released for every 1.00 g sucrose oxidized?

**Learning activity # 4**

Title of Learning Activity: Introduction to Organic Chemistry

**Specific Teaching and Learning Objectives:**

At the end of this learning activity you should be able to:

- Classify types of organic compound based on functional groups
- Name different classes of organic compounds using IUPAC nomenclature
- Write structural formulae and isomers
- Relate properties and reactions of organic compounds to functional groups

**Summary of the learning activity:**

This learning activity is the last unit of this module. In this learning activity important explanations on the classification of organic compounds, the IUPAC method of naming organic compounds, isomers and functional groups are given. At the end of each section there are exercises which you need to work on.
At the end of the unit multiple choice questions are given. These questions are meant to assess your understanding of the unit.

**List of relevant readings:**


**List of relevant resources:**

- Computer with Internet facility to access links and relevant copy-write free resources.
- CD-Rom accompanying this module for compulsory readings and demonstrations.
- Multimedia resources like video, VCD and CD players.

**List of relevant useful links:**


2. Virtual Chembook, by Charles E. Ophardt and Elmhurst College (Chapters on a) Hydrocarbon compounds - Alkanes, Alkenes, Alkynes, Cyclic, Aromatic b) Organic Names - Summary and Major Functional Groups)
3. ScienceWorld, by Eric Weisstein (Chapter on organic chemistry covers nomenclature)

In the links given below you will find exams with answers that enable you assess the level of your understanding of the unit.

Detailed description of the activity:

Organic chemistry is the study of carbon compounds. Carbon atoms link together to form long chains and rings. Carbon as an element has the ability to form millions of compounds. When other elements are connected to this, compounds of complex structure are formed. Because of this property of carbon, there are more carbon compounds than the number of compounds of all other elements.

In organic chemistry therefore, compounds are classified into different families and their general properties and reactions are studied. Families of carbon compounds contain innumerable members. Each of them exhibit the general properties of the family as well as some properties which are special to them.

The class of compounds that forms the framework of all organic compounds is hydrocarbons. Hydrocarbons are compounds which are made up of only two elements, hydrogen and carbon. Hydrocarbons are divided into two main classes according to their structure – aliphatic and aromatic. Aliphatic hydrocarbons are those hydrocarbons which do not contain the benzene group, or the benzene ring, whereas aromatic hydrocarbons are those which contain one or more benzene rings. Aliphatic hydrocarbons are further divided into alkanes, alkenes, and alkynes. An alkane in the shape of a ring is called a cycloalkane. Cycloalkanes have the general formula CnH2n.

Alkanes have the general formula CnH2n+2, where n = 1, 2, 3, …… Alkane hydrocarbon molecules contain only single covalent bonds. In these compounds the bonds are said to be saturated. Thus, alkanes are known as saturated hydrocarbons and this property makes them quite un-reactive.

An alkene is a compound that has at least one double bond. Straight-chain alkenes with one double bond have the same formula as cycloalkanes, CnH2n. A double bond, involves two pairs of electrons. In a double bond, one pair of electron forms a single bond and the other pair forms an additional, weaker bond. The electrons in the additional, weaker bond react faster than the electrons in the single bond. Due to this fact, carbon-carbon double bonds are more reactive than carbon-carbon single bonds. In an alkene reaction, the reaction almost always occurs at the site of the double bond. The reactive double bond is the functional group for an alkene.

An alkyne is a compound that has at least one triple bond. A straight chain alkyne with one triple bond has the formula CnH2n-2. Triple bonds are even more reactive than double bonds. The functional group for an alkyne is the triple bond.

Exercise

Identify the compounds given below as an alkane, a cycloalkane, an alkene, or an alkyne

EMBED ChemDraw.Document.6.0

 Cyclopentane, C5H10

CH3CH=CH2

propene, C3H6
Learning Activities

(a) \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \]  
butane, C\text{4H10},

(b) \[ \text{CH}_3=\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \]  
2-hexyne, C\text{6H10}

(c) 

(d) 

The figure below gives the structures of ethane, propane and butane.

![Structures of ethane, propane, and butane](image)

Exercise

a) How many structural isomers can be identified for pentane, C\text{5H12}?

b) Draw the structures of all the possible isomers.

The structures of ethane and propane are straightforward, for there is only one way to join the carbon atoms in these molecules. However, butane has two possible bonding schemes and can exist as structural isomers called n-butane (where n stands for normal) and isobutane. Molecules that have the same molecular formula, but different structures are known as structural isomers.

In the alkane series, as the number of carbon atoms increases, the number of structural isomers increases rapidly. For example, butane has two isomers; decane, C\text{10H22}, has 75 isomers; and the alkane C\text{30H62} has over 400 million isomers. Most of these isomers do not exist in nature and have not been synthesized.

The International Union of Pure and Applied Chemistry (IUPAC) has set standard rules for naming organic compounds. Why the need for IUPAC nomenclature? State the reasons. The systematic names of alkanes and most other organic compounds follow the same pattern, shown below.
The root of a compound's name indicates the number of carbon atoms in the main (parent) chain or ring. The roots for hydrocarbon chains that are up to ten carbons long are:

- C1 - Meth
- C2 - Eth
- C3 - Prop
- C4 - But
- C5 - Pent
- C6 - Hex
- C7 - Hept
- C8 - Oct
- C9 - Non
- C10 - Dec

To determine which root to use, the carbons in the main chain or main ring of the compound are counted. If the compound is an alkene or alkyne, the main chain or ring must include the multiple bond. See the examples given in fig.4.3.

Figure 4.3 (A) There are six carbon in the main chain. The root is then –hex-. (B) There are five carbons in the main ring. The root is then –pent-.

The suffix indicates the type of compound, according to the functional groups present. The suffix for alkanes is –ane, for alkenes –ene, and for alkynes –yne. Thus an alkane composed of six carbon atoms in a chain is called hexane. An alkene with three carbons is called propene.

The prefix indicates the name and location of each branch and functional group on the main carbon chain. Most organic compounds have branches, called alkyl groups, attached to the main chain. An alkyl group is obtained by removing one hydrogen atom from an alkane. To name an alkyl group, change the –ane suffix to –yl. For example, - CH3 is the alkyl group that is derived from methane, CH4. It is called the methyl group, taken from the root meth -.

To name hydrocarbons follow the steps given below.

Find the root: Identify the longest chain or ring in the hydrocarbon. For an alkene or an alkyne, make sure that the longest chain or ring you identified includes the multiple bond/s. To obtain the root, count the number of carbon atoms in the main chain. For a cyclic compound, add the prefix – cyclo- before the root.

Find the suffix: Use the suffix – ane for an alkane; -ene for an alkene, - yne for an alkyne. If more than one double or triple bond is present, use the prefix di- for two or tri- for three..... double or triple bonds before the suffix to indicate the number of multiple bonds.
Learning Activities

Give a position number to the carbon atoms in the main chain. If there is no double or triple bond, number the compound so that the branches have the lowest possible position numbers. If there is a double or a triple bond, start from the end that gives you the lowest possible position number for the double or triple bond.

Find the prefix: Name each branch as an alkyl group, and give it a position number. If more than one branch is present, write the names of the branches in alphabetical order. Put the position number of any double or triple bonds after the position numbers and names of the branches, just before the root. Note: Use the carbon atom with the lowest position number to give the location of a double or triple bond.

Put the name together: prefix + root + suffix.

Exercise

Give the IUPAC names of the following alkanes.

Note: In the CD accompanying this module read the examples given in the files “6-OrgCpdsNamingandIsomerism” and “8-hydrocarbons” before you do the questions given in this activity.

Most organic compounds can be divided into relatively few classes according to the functional groups they contain. A functional group is the part of a molecule having a special arrangement of atoms that is largely responsible for the chemical behavior of the parent molecule. Different molecules containing the same kind of functional group or groups react similarly. Thus, by learning the characteristic properties of a few functional groups, we can study and understand the properties of many organic compounds.

All alcohols contain the hydroxyl group, -OH. Following are some examples of common alcohols:

- Methanol
- Ethanol
- 2-propanol
- Ethylene glycol

To name an alcohol, name the parent chain. For example, Eth- when the alcohol contains two carbon atoms, Prop- when it contains three carbon atoms etc. If the parent chain is a saturated hydrocarbon the prefix ‘-ane’ should be added.
Finally to indicate the alcoholic functional group ‘ol’ has to be added indicating its position when the number of carbon atoms in the main chain is more than 3. For example in the alcohol

\[
\text{OH} \\
H_3C\text{CHCH}_3
\]

the parent chain is an alkane containing 3 carbon atoms. The OH group is positioned on carbon number 2. Thus, it is named as 2-propanol.

**Exercise**

Name the compounds

(a) CH3-CH2-CH2-OH  
(b) CH3-CH2-CH(OH)-CH2-CH2OH

Ethers contain the R-O-R’ linkage, where R and R’ are either alkyl or aryl groups.

**Examples,**

\[
\text{H}_3\text{C} \text{O} \text{CH}_3 \quad \text{H}_3\text{C}-\text{H}_2\text{C-O-CH}_2\text{-CH}_3
\]

Dimethyl ether  
Diethyl ether

In naming ethers, the shortest alkyl chain is named together with the oxygen atom as an alkoxy group followed by the name of the longest alkyl chain as the root. For example in, CH3-O-CH2-CH3, the shortest alkyl group is the methyl, CH3, group. Thus, the CH3-O-group is named as ‘Methoxy’. The longest alkyl group is the ethyl, -CH2-CH3, group. Then, CH3-O-CH2-CH3 is named as ‘Methoxy ethane’. 
Exercise

Do the matching activities given on page 78 of the PDF file ‘6-Naming & Isomerism’.

Both aldehydes and ketones possess the carbonyl group, >C = O. The difference between aldehydes and ketones is that in aldehydes at least one hydrogen atom is bonded to the last carbon of the carbon chain to which oxygen is bonded by a double bond, whereas in ketones no hydrogen atoms are bonded to this carbon atom. The functional groups for an aldehyde and a ketone are given below.

\[
\begin{align*}
\text{(R = alkyl or aryl group)} \\
\text{Fig. 4.4 (a) Aldehydic functional group (b) Ketonic functional group}
\end{align*}
\]

Examples

In naming an aldehyde, give the carbon atom of the carbonyl group the position number 1 and name the parent alkane.

To indicate that the compound is an aldehyde, replace the –e at the end of the name of the parent alkane with –al. There is no need to include a position number for the carbonyl group since it is always given position number 1.

To name a ketone, name the parent alkane which contains the C = O group. To indicate that the compound is a ketone, replace the –e at the end of the name of the parent alkane with –one if the compound contains one ketone group. If there are more than one ketone groups, keep the –e suffix and add a suffix such as –dione for two, -trione for three ketonic groups.

For carbon chains that have more than four carbons, a position number is needed for the carbonyl group. In this case, number the carbon chain so that the carbonyl group has the lowest possible number.

Carboxylic acids are compounds with –COOH groups.

Following are some examples of carboxylic acids.
Multiple choice questions.

Four choices are given under each of the questions given below. Among the choices provided under a given question choose the one which best answers the question and underline the letter corresponding to your choice.

1. The class of organic compounds described as hydrocarbons are
   a) all compounds which contain saturated carbon-hydrogen bonds.
   b) those compounds which are made up of the elements carbon and hydrogen only and which do not contain a cyclic group.
   c) are compounds which are made up of hydrogen and carbon and which may or may not contain a benzene ring.
   d) all compounds containing carbon and hydrogen.

2. Aromatic hydrocarbons are
   a) all cyclic hydrocarbons.
   b) hydrocarbons which consist benzene rings only.
   c) hydrocarbons which contain a benzene ring in their structure.
   d) cycloalkanes

3. Which formula represents an alkyne?
   a) C2H6   b) C3H6   c) C4H8   d) C5H8

4. Structural isomers have
   a) the same empirical and molecular formula
   b) the same physical and chemical properties
   c) different general formulas
   d) the same arrangement of their atoms.

Questions 5-16 pertain to the following structures.
5. The structures which are examples of alcohols are
   a) a, b, c and d  c) b and c
   b) a, c and d     d) all except e

6. Which of the structures is an example of an aromatic hydrocarbon?
   a) g, h and i     b) h and i     c) only h     d) only i

7. Which of the structures are examples of a hydrocarbon?
   a) all           b) g, h and i     c) g and h     d) only g

8. The structures representing a carboxylic acid are?
   a) a, c, d, e and f  b) a, b and e  c) e and f  d) only e

9. The structure representing an ether are?
   a) a, b and e     b) a, b, c, d, e and f  c) only b  d) only e

10. The structures representing an aldehyde are?
    a) a, b, c, d, e and g  b) a and e  c) only a  d) only b

11. The structures representing a ketone are?
    a) a, b, c, d, e and g  b) a and e  c) only a  d) only b
12. Which structure is an example of a saturated hydrocarbon?
   a) g, h and i   b) only h   c) g and i   d) only i

13. The structure of ethoxy butane is
   a) a   b) d   c) e   d) b

14. The structure representing 2-butanol is?
   a) a   b) c   c) d   d) f

15. The IUPAC name of the structure represented by the structure ‘g’ is
   a) 3,5-heptadiene   b) 2,4-heptene   c) 2,4-heptadiene   d) 3,5-heptene

**Synthesis of the Module**

This module is the second module in general chemistry. The entire module comprises four units. The first unit covers topics on reaction rates, order of a reaction, the factors that affect reaction rates and chemical equilibrium.

As a continuation of the discussions on the properties associated with the three states of matter in general chemistry I module, in the second unit of this module we examine the properties of solutions focusing mainly on the role of intermolecular forces in solubility and other physical properties of solutions including their units of concentration. Some basic concepts on solubility, and colligative properties of solutions are also highlighted in the second unit.

When substances undergo chemical reactions and form products, there is always an accompanying change in the energies of the reactants. This vital aspect of heat changes in different types of chemical reactions is the topic covered in the third unit of this module.

The fourth unit covers introductory organic chemistry. It deals mainly with the classification and IUPAC nomenclature of organic compounds and how these classes of organic compounds can be distinguished according to the functional groups they contain.

At the end of each topic in a unit worked examples are given to provide a clear consistent methodology that you can follow to develop conceptual and quantitative problem solving skills. Exercises are given at the end of a unit which you will be required to work through, on completing the various readings.
Summative Evaluation

Multiple choice questions

For each of the following multiple choice questions, underline the letter corresponding to your choice among the four choices given under the question.

1. Which of the following statements is wrong about solutions?
   a) When a solution is saturated, dissolving and precipitation occur at the same rate.
   b) A solute tends to dissolve in solvents that are chemically similar.
   c) The solubility of gases is affected by pressure.
   d) Colligative properties of solutions depend only on solute concentration.

2. The rate law for the decomposition of N2O5 is given by; Rate = K[N2O5]. If K = 1.0x10^-5, what is the reaction rate when the N2O5 concentration is 0.001 mol/L?
   a) 10^-5 mol/L.s  c) 10^-2 mol/L.s
   b) 10^-8 mol/L.s  d) 10^4 mol/L.s

3. Transition from the liquid to the gaseous state
   a) is an exothermic process
   b) is an endothermic process
   c) involves no enthalpy change
   d) could be an endothermic or exothermic process

4. The rate of a chemical reaction may be influenced by
   a) the concentration of the reactants
   b) the physical nature of the reactants
   c) the presence of a catalyst
   d) all of the above

5. Which of the following is not a solution?
   a) a mixture of CO2 and H2 gases
   b) sugar dissolved in water
   c) Salt dissolved in water
   d) none of the above
6. In a given liquid-liquid solution the solvent is
   a) the component which is larger in volume
   b) the more polar liquid
   c) the component which is smaller in volume
   d) the more non-polar liquid

7. The molarity of a solution made by dissolving 4.0 g of 100% H2SO4 (density = 1.8 g cm-3) in 120 g of water is,
   a) 0.86 M   b) 0.0061 M   c) 0.33 M   d) none

8. Which of the following equilibrium constants has the biggest relative amount of products?
   K = 1
   K = 0
   K = 0.0005
   K = 2,000 The largest equilibrium constant has the largest relative amount of product

9. Which of the following properties of solutions is dependent on the chemical nature of the solute?
   a) solubility   c) vapour pressure
   b) osmotic pressure   d) boiling point

10. If heat is absorbed during a solubilization process
    a) solubility increases with an increase in temperature
    b) solubility decreases with an increase in temperature
    c) solute-solvent interaction is stronger than solute-solute and solvent-solvent interaction.
    d) b and c are correct.

11. In a reversible reaction,
    a) the rate of the forward reaction goes on increasing until the reaction reaches equilibrium and remains constant then after
    b) the rate of the reverse reaction goes on decreasing after equilibrium
c) the concentration of reactants and products will be equal at equilibrium.

d) the rate of the reverse reaction goes on decreasing upto equilibrium and
remains constant from then on.

12. Which pair of concentration units is not affected by temperature change on the
solution?

a) mole fraction and molarity       c) Mass percent and molarity
b) Mass percent and molality        d) Molarity and molality

13. Which formula represents an unsaturated hydrocarbon?

a) C2H6       b) C4H10       c) C3H6       d) C5H12

14. The name of a compound with the general formula R-OH could be

a) Ethanol       b) Methane       c) Ethanoic acid       d) Methyl methanoate

15. The two carbons joined by a triple bond in an alkyne are connected by

a) three sigma bonds;

b) one sigma bond and two pi bonds;

c) three pi bonds;

d) two sigma and one pi bond.

16. Which of the structures below is not in isomer of hexane?

(a) 

(b) 

(c) 

(d)
Questions 17-20 pertain to the following structures.

(a) (b) (c) (d) (e)

17. An example of which of the following is not included in the structures?
   a) ketone   b) aldehyde   c) ether   d) carboxylic acid

18. The structures which are examples of alcohols are
   a) a, b, c and d   c) b and c
   b) a, c and d   d) all except e

19. Which structure is an example of a hydrocarbon?
   a) b and c   c) only e
   b) b, c and e   d) all the structures

20. Which of the structures is an example of a carboxylic acid?
   a) a, b, c and d   c) only d
   b) a, c and d   d) only c

References

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Academic background

B.Sc in Chemistry; Asmara University, Asmara, Eriteria (1985)

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Dr. Dejene has taught various chemistry courses at Jimma University in Ethiopia. He has served as department head and currently he is dean of the faculty of Education at the same University.