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I. Chemistry 5, physical chemistry 1
by Dr. Onesmus M. Munyaki

II. Prerequisite Courses or Knowledge
The learner should have covered Energy and Chemical Reactions in Unit III in the Module Chemistry 2: Introductory Chemistry. The learner should be able to:

- Distinguish between exothermic and endothermic reactions and draw their reaction profiles
- Do stochiometric calculations involving heat changes
- Explain the concept of enthalpy and perform calculations using it
- Predict spontaneity of chemical reactions based on enthalpy, entropy and Gibbs free energy qualitatively and quantitatively
- Do calculations involving energy changes occurring in chemical reactions
- Write and interpret a rate law given the rate determining step
- State and explain factors that control reaction rates

III. Time
120 hours

<table>
<thead>
<tr>
<th>Topic</th>
<th>Approximate Time (hours)</th>
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<tbody>
<tr>
<td>Kinetic Theory of Gases</td>
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<td>Thermochemistry</td>
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<td>Spontaneity in Chemical Processes</td>
<td>30</td>
</tr>
<tr>
<td>Chemical kinetics</td>
<td>25</td>
</tr>
</tbody>
</table>

IV. Material
In order to successfully complete this module, learning activities will require Internet connectivity to enable

- Access of learning activities online
- Online assessment in form of quizzes, tests, assignments and experiments
- Multimedia interaction (including video conferencing)
- e-Library and data base utilisation
• Interactive group discussions/chat sessions
• Access to a library and self-study centre
• Access to recommended textbooks and reference materials (web-based learning materials)

V. Module Rationale

Physical chemistry is the study of the underlying physical principles that govern the properties and behaviour of chemical systems. The knowledge of these principles is important and provide a framework for all branches of chemistry, whether we are synthesizing compounds in a research laboratory, manufacturing chemicals on an industrial scale or trying to understand the intricate biological processes in the cell. This module is intended to broaden your understanding of physical principles in chemistry. It deals with three main areas: thermodynamics, quantum chemistry and chemical kinetics. Studying thermodynamics enables the chemist to predict whether or not a reaction will occur when reactants are brought together under a specific set of conditions. Indeed industrial chemists often place more emphasis on speeding up the rate of a reaction than on its percentage yield. Organic chemists use kinetic studies to determine the mechanisms of reactions and to tell how fast products will be formed.

VI. Content

6.1. Overview

This module is about advanced concepts in physical chemistry that cover the topics of thermodynamics, chemical kinetics, and kinetic molecular theory. In our study of thermodynamics (thermodynamics comes from the Greek words for “heat” and “power”), we shall be looking at the first and second laws of thermodynamics as they apply to volume-pressure processes and energy changes associated with chemical reactions. The topics in chemical kinetics will look at rate laws and factors affecting the rates of chemical reactions. In molecular kinetic theory, we shall be looking at explaining the general behaviour of gases from a molecular point of view.
6.2 Outline

The five units to be covered in this module are each made up of the following topics:

**Unit I: Kinetic Theory of Gases (20 hours)**
- Assumptions of the Kinetic Theory
- Predictions of Kinetic Theory
- Molecular Speeds and Distribution

**Unit II: Thermodynamics (30 hours)**
- Fundamental Aspects of the First Law
- Basic Concepts
- Work, Heat and Energy
- Statement of the First Law
- State Functions
- Constant Volume and Constant Pressure Processes

**Unit III: Thermochemistry (15 hours)**
- Standard Enthalpy Changes
- Enthalpy of Chemical Change: Enthalpy of Reaction
- Enthalpy of Physical Transformation
- Hess’ Law

**Unit IV: Spontaneity in Chemical Processes (30 hours)**
- The Second Law of Thermodynamics
- Relationship between Entropy and Spontaneity
- Free Energy and Equilibrium

**Unit V: Chemical kinetics (25 hours)**
- Rates of Chemical Reactions
- Measuring of Reaction Rates
- Rate of Reaction
- Integrated Rate Laws
- Temperature Dependence of Reaction Rate
6.3 Graphic Organizer

Physical Chemistry 1

Unit I Kinetic molecular theory

Unit II Thermodynamics

Unit III Thermochemistry

Unit IV Spontaneity in chemical processes

Unit V Chemical kinetics
VII. General Objective(s)

On completion of this module the learner should be able to:

- Explain the behaviour of gases using the kinetic molecular theory
- Carry out computations involving gas law problems
- Calculate the magnitude of energy released or absorbed in chemical reactions
- Predict whether the entropy change of the system in a given reaction is positive or negative
- Identify qualitatively, entropy changes associated with physical and chemical processes
- Predict the spontaneity of chemical process direction
- Use the Gibbs free energy equation to (a) predict the spontaneity of a process and (b) to explain the effect of change in enthalpy, entropy and temperature on a chemical reaction
- Explain and define the terms favourable for spontaneous change: entropy, second law of thermodynamics and free energy
- Apply the concepts learnt in the module to solve and explain practical problems found in the real world
### VIII. Specific Learning Objectives
(Instructional Objectives)

#### Unit I: Kinetic Theory of Gases
- Assumptions of the kinetic theory
- Predictions of kinetic theory
- Molecular speeds and distribution

At the end of this unit the learner should be able to:
- State and explain the assumptions of kinetic theory as applied to gases
- Explain the properties of gases using kinetic theory
- Explain the manner in which the behaviour of a real gas differs from that of an ideal gas
- Use the kinetic theory to account for the gas laws
- Derive the equation \( P = \frac{1}{3} N m \langle v \rangle^2 \) that explains the pressure of a gas from a molecular viewpoint
- Carry out calculations related to pressure, volume or temperature changes involving the gas laws and the ideal gas equation

#### Unit II: Thermodynamics
- Fundamental aspects of the first law
- Basic Concepts
- Work, Heat and Energy
- Statement of the First Law
- State Functions
- Constant Volume and Constant Pressure Processes

At the end of this unit the learner should be able to:
- Define the terms: system, surroundings, open system, closed systems and isolated system
- Define and explain the concepts of heat, work and energy
- State the first law of thermodynamics and apply it solving problems related to chemical process
- Differentiate between state functions and non state functions
- Distinguish between enthalpy and thermal energy
- Describe, explain and relate the first law of thermodynamics to chemical reactions taking place at constant pressure or volume.
Unit III: Thermochemistry

- Standard Enthalpy Changes
- Enthalpy of Chemical Change: Enthalpy of reaction
- Enthalpy of physical Transformation
- Hess’s Law

At the end of this unit the learner should be able to:

- Explain that chemical changes are accompanied by energy changes principally in the form of thermal energy
- Define the terms exothermic and endothermic process
- Describe how changes in enthalpy and thermal energy accompanying a chemical reaction can be measured calorimetrically
- Define bond energy. Use tables of bond energies to estimate the enthalpy of a reaction
- Write and manipulate \textit{thermochemical equations}
  - Combine a set of step thermochemical equations to obtain a net thermochemical equation (\textit{Hess’s Law})
  - Write thermochemical equations for combustion and formation reactions

Unit IV: Spontaneity in Chemical Processes

- Spontaneity in Chemical Processes
- The Second Law of Thermodynamics
- Relationship Between Entropy and Spontaneity
- Free Energy and Equilibrium

At the end of this unit the learner must be able to:

- Explain what is meant by a spontaneous process
- Define the term entropy
- Explain the second law of thermodynamics
- Make qualitative prediction of direction of reaction based on entropy
- Define the term free energy and explain how it is related to equilibrium properties
- Use Gibbs free energy to predict whether a reaction will be spontaneous or not
Unit V: Chemical kinetics

- Rates of a Chemical Reactions
- Measuring of Reaction Rates
- Rate of Reaction
- Integrated Rate Laws
- Factors Affecting Rates of Reaction

At the end of this unit the learner must be able to:

- Explain and use the terms: rate of a reaction, rate law of a reaction, order of a reaction, rate constant, half-life of a reaction, rate determining step
- Write the reaction rate expressions of chemical reactions
- Predict how changes in the conditions affect the rate of a chemical reaction
- Determine the order of reaction from experimental data
IX. Teaching and learning activities

9.1 Pre-assessment

Title of Pre-assessment

Foundation principles for understanding thermodynamics, kinetic theory and chemical kinetics

Rationale

The pre-assessment has been designed to determine what you already know about some fundamental physical science concepts that are key to the successful completion of this module. Questions range from basic gas law concepts and principles whose knowledge will be required for learning the kinetic theory section of the module to concepts involving heat changes during chemical reactions. The latter concepts are necessary for understanding thermodynamics and chemical kinetics.

Questions

1. Which of the following is the correct description of an exothermic process?
   (a) A chemical process in which thermal energy is released to the surroundings
   (b) A process in which there is an increase in the degree of disorder
   (c) A chemical process in which heat energy is absorbed from the surroundings
   (d) A chemical process in which heat is neither absorbed nor released

2. The volume of a fixed amount of gas at constant pressure is directly proportional to temperature (absolute) is a statement of which law?
   (a) Charles Law
   (b) Boyles Law
   (c) Grahams Law
   (d) Combined gas Law
3. Which of the following curves is a correct representation of the pressure-volume versus pressure graph for a fixed mass of an ideal gas at constant temperature?

(a) ![Graph A]  (b) ![Graph B]  (c) ![Graph C]  (d) ![Graph D]

4. The kinetic data from a certain reaction are plotted and they yield a straight line. The reaction proves to be second order. The labels for the x and y-axes, respectively, are:
   (a) Plot of t vs 1/[A]
   (b) Plot of [A] vs t
   (c) Plot of t vs ln[A]
   (d) Plot of 1/[A] vs t

5. Which of the following will have no effect on the rate of reaction?
   (a) presence of a catalyst
   (b) physical state
   (c) concentration
   (d) polarity

6. The graph shows the Boltzmann distribution of molecular speeds.

Which one of the following statements is not correct?
   (a) Raising the temperature always decreases the number of molecules with faster speeds within a given volume.
   (b) The area under the curve is proportional to the number of molecules present.
7. The diagram below is a representation of a hill. A and B represent two routes used by a climber to reach the top of the hill.

Which of the following statements is not true?

(a) The change in potential energy is the same irrespective of the path taken.
(b) Different amount of work is done using path A and B.
(c) If the climber goes from state 1 to state 2 and back to state 1, the potential energy returns to its initial value.
(d) The change in potential energy would be different if the climber was air lifted from the bottom of hill to the top of the hill.

8. A body builder has weight-lifting has part of her weight control regime. She lies on her back and lifts dumb bell shaped weights of 10 kg through a height of 60 cm. How much energy is expended if she lifts the weights 10 times?

(a) 15 J
(b) 10 J
(c) 600 J
(d) 25 J

9. A system is defined as that part of the universe that we choose to study and is classified according to its interaction with the surroundings. A cup of coffee is recognised as a thermodynamic system and is classified as a

(a) Closed system
(b) Open system
(c) Isolated system
(d) Surroundings
10. Which statement about the effect of a catalyst on a reversible reaction is correct?

(a) It increases the equilibrium constant on the forward reaction
(b) It increases the yield of the product in an equilibrium
(c) It decreases the rate constant for both the forward and reverse reaction
(d) It increases the rate of reaction of the forward and reverse reaction

**Title of Pre-assessment**

Foundation principles to understanding thermodynamics, kinetic theory and chemical kinetic

**9.2 Answer key**

1. (a)
An exothermic process is one that produces a temperature increase in an isolated or non-isolated system, and gives off heat to the surroundings

2. (a)
Charles’s law state that the volume of a fixed amount of gas at constant pressure is directly proportional to the absolute temperature. In mathematical terms, it may be expressed as \( V \propto T \) or \( V = bT \). The value of the constant \( b \) depends on the amount of gas and pressure.

3. (c)
\( PV = nRT \) is constant therefore the curve is a horizontal line. Plot in C.

4. (d)
The rate law for a second order reaction is given by
rate of change of \([A]\) = \(k[A]^2\)

The integrated form of the equation is of the form \( \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \)
A plot of \( \frac{1}{[A]_t} \) versus \( t \) yields a straight line.

5. (d) 
polarity – has no effect on the rate of reaction

6. (a) 
The first statement is not correct since increasing temperature actually increases the number of molecules with faster speeds and reduces those of lower speeds.

7. (d) 
Potential energy is a state function and does not depend on path taken.

8. (c) 
In lifting the dumb bell she will do work against the force of gravity. The work done in this case is

\[
\text{Force} = \text{mass} \times \text{acceleration} = 10 \, \text{kg} \times 10 \, \text{m} \, \text{s}^{-2} = 100 \, \text{kg} \, \text{m} \, \text{s}^{-2}
\]
\[
\text{Work} = \text{force} \times \text{distance} = 100 \, \text{kg} \, \text{m} \, \text{s}^{-2} \times 0.6 \, \text{m}
\]
\[
= 60 \, \text{kg} \, \text{m}^2 \, \text{s}^{-2} = 60 \, \text{J for each lift.}
\]
For ten times work done = 60 J \times 10 = 600 J

9. (b) 
An open system is one in which both matter and energy can be exchanged between the system and the surroundings. In this case, matter is lost in the form of vapour and heat as thermal energy.

10. (d) 
A catalyst speeds up a reaction usually by lowering the value of the activation energy for both the forward and reverse reactions to the same extent. A catalyst can be recovered unchanged at the end of the reaction.
9.3 Pedagogical Comment for Learners

The assessment test should give you some indication of what content knowledge you are expected to cover in this module. Your performance will also help you to identify areas of knowledge you may want to focus on, or items of information that will require special attention. For example, you may notice that you need to be especially careful about the signs, symbols and units when doing the calculations in this module; and that Absolute (Kelvin) temperature must be used with all the gas laws in which temperature is a factor. The learner who has scored less than 40 percent is likely to encounter significant difficulties in this module. It is advisable that such a learner revisit the pre-requisite module, Chemistry 2.
X. **Key Concepts (Glossary)**

**Absolute temperature scale.** This refers to a temperature scale that uses the absolute zero of temperature as the lowest temperature.

**Absolute zero.** The lowest temperature theoretically attainable. It is the temperature at which the kinetic energy of atoms and molecules is minimal.

**Adiabatic boundary.** A boundary that does not permit energy transfer as heat.

**Avogadro’s law.** At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present.

**Bomb calorimeter.** A calorimeter in which there is no net loss of heat from the calorimeter to the surroundings. It is used to measure the heat of a combustion reaction. The measured heat of reaction at constant volume, \( q_v = \Delta E \).

**Boyle’s law.** The volume of a fixed mass of a gas maintained at constant temperature is inversely proportional to the gas pressure.

**Calorimeter.** A device for measuring the heat transfer.

**Charles’s law.** The volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature.

**Closed system.** A system with a boundary through which matter cannot be transferred.

**Dalton’s law.** The total pressure of a mixture of gases is just a sum of the pressures that each gas would exert if it were present alone.

**Diffusion.** The spreading of a substance (usually a gas) into a region where it is not originally present due to the random motion of the molecules.

**Dipoles.** A pair of separated opposite charges. The dipole moment (\( \mu \)) is the product of the positive charge and the distance separating the charges.

**Endothermic process.** A process that absorbs energy as heat from its surroundings.

**Energy.** The capacity to do work.

**Enthalpy (\( H \)).** A thermodynamic quantity used to describe heat changes taking place at constant pressure, \( H = E + PV \).

**Enthalpy change.** The heat (under certain familiar conditions) involved in a process; symbolized \( \Delta H \). At constant pressure, \( \Delta H = \Delta E + P\Delta V \).

**Entropy (\( S \)).** A direct measure of the degree of disorder or randomness of a system.
**Equilibrium.** A condition in which an infinitesimal change in a variable in the opposite direction results in opposite change in the state. In chemical reactions, it represents the situation in which the reactants and products are producing each other at the same rate.

**Exothermic process.** A process that releases energy as heat.

**Free energy (G).** The energy available to do useful work. Defined by \( G = H - T\Delta S \). Changes in free energy are useful in indicating the conditions under which a reaction will occur.

**First law of thermodynamics.** Energy can be converted from one form to another but can not be created or destroyed.

**Gibbs Free Energy.** See free energy.

**Heat capacity.** The quantity of heat required to change the temperature of a substance by one degree usually expressed as \( J^\circ C^{-1} \) or \( cal^\circ C^{-1} \).

**Heat of reaction.** The energy change accompanying a chemical reaction.

**Heat.** The transfer of energy as a result of a temperature difference.

**Hess’s law.** The law that states that the enthalpy change for an overall or net process is the sum of enthalpy changes for the individual steps in the process.

**Ideal gas.** A hypothetical gas whose pressure-volume-temperature behaviour can be accounted for by the ideal gas equation.

**Ideal gas constant (R).** The numerical constant appearing in the ideal gas equation. The constant has a value of 0.0821 L atm mol\(^{-1}\) K\(^{-1}\) or 8.314 J K\(^{-1}\) mol\(^{-1}\). An ideal gas (perfect gas) is a hypothetical gas that obeys the ideal gas equation.

**Ideal gas equation.** An equation expressing the relationship between pressure, volume, temperature, and amount of gas. Mathematically stated as \( PV = nRT \), where \( n \) is the number of moles, \( P \) is the pressure of gas and \( V \) the volume of gas.

**Internal energy.** Total energy of the system; symbolized by \( E \). The sum of all the kinetic energies and potential energies of the particles within the system.

**Isobaric calorimeter.** A calorimeter for the studying processes at constant pressure.

**Isolated system.** A system with a boundary through which neither matter nor energy can be transferred.

**Kelvin (temperature).** The SI base unit of temperature. The Kelvin temperature is an absolute temperature. The lowest attainable temperature is 0 K = -273.15 \( ^\circ C \). It is related to the Celsius temperature through the expression \( T (K) = T(^\circ C) + 273.15 \).
Kinetic-molecular theory of gases. The treatment of gas behaviour in terms of random motion of molecules. It is a model used for describing gas behaviour based on a set of assumptions.

Open system. A system with a boundary through which both matter and energy can be exchanged with the surroundings.

Potential energy. The energy due to the position or arrangement. Associated with forces of attraction and repulsion.

Pressure-volume work. The work associated with the expansion or compression of gases.

Root-mean-square-velocity. The square root of the average of the squares of speeds of all molecules in a sample.

Specific heat. The quantity of heat required to change the temperature of one gram of substance by one degree Celsius.

Standard conditions of temperature and pressure. Refers to conditions at a temperature of exactly 273.15 K (0 °C) and a pressure of 101325 Pa (1 atm or 760 mmHg).

Standard enthalpy of formation. The heat change involved when 1 mol of the substance is made from its elements in their standard state; symbolized $\Delta H^\circ_f$.

Standard enthalpy of reaction. The enthalpy change when a reaction is carried out under standard states conditions.

Standard enthalpy. The change in enthalpy for a process in which the initial and final substances are in their standard state, symbolized $\Delta H$.

Standard temperature and pressure (STP). At 273 K (0 °C) and 101325 Pa (1 atm).

State function. Property that depends only on the current state of the system and is independent of how that state has been prepared. A function that depends only on the initial and final states of the system.

Surroundings. The part of the world outside the system where we make our measurements.

System. Part of the world in which we have specific interest.

van der Waals equation. An equation used to describe the $P$, $V$, and $T$ of a non-ideal gas.

van der Waals forces. A term used to describe the dipole-dipole, dipole-induced dipole and dispersion forces

Work. The transfer of energy by motion against an opposing force.
XI. Compulsory readings

Reading #1

Complete reference: Properties of gases
Chem1 Virtual Text Book
URL: http://www.chem1.com/acad/pdf/c1gas.pdf
Date Accessed 26 August 2006

Abstract
This text introduces the properties of gases as exhibited in the gas laws. It then uses the kinetic model to explain and justify the behaviour of gases from a molecular viewpoint.

Rationale
If gases do exist as particles then they must be explainable on this basis – kinetic molecular model. This reading is essential for the understanding of learning content in Unit I of this module. It introduces the gas laws followed by a kinetic explanation and justification for them. This topic is covered in Sections 5 – 7 of the text.

Reading #2

Complete reference: Chemical energetics
http://www.chem1.com/acad/webtext/virtualtextbook.html
Date Accessed 26 August 2006

Abstract
This document introduces the learner to the fundamental concepts of thermodynamics. It begins by defining terms such as energy, the various types of energy (kinetic and potential energy) and units of energy. It then goes on to explain the conceptual knowledge for understanding thermodynamics. It goes further to look at the interconversion of energy as it tackles the first law of thermodynamics and its applications: in thermochemistry (energy changes in chemical reactions), thermochemical reactions, bond energies, energy content of foods and fuels.

Rationale
Energy changes are critical to an understanding of many of the concepts encountered in this module. This document therefore is critical reading for Unit II and Unit III of the module. Concepts initially developed in Unit II are applied in Unit III in studying the energy changes involved in chemical reactions.
Reading #3

Complete reference: Thermodynamic equilibrium
http://www.chem1.com/acad/webtext/virtualtextbook.html

Date Accessed 26 August 2006

Abstract
The reference text covers aspects of the drive towards chemical change in terms of spreading of energy through entropy and Gibb's free energy. Concepts are developed from a molecular point of view to explain physical phenomenon. Factors that favour spontaneity of processes and the condition for equilibrium are discussed.

Rationale
Thermodynamic equilibrium is essential to understanding why reactions are spontaneous and how far they go. Spontaneity is the subject of Unit IV and is well covered by this reference text. Concepts developed earlier in Unit II are used in studying factors that promote spontaneity of chemical change.

Reading # 4

Complete reference: Gas laws

Abstract
This text covers the basics of the properties of gases. It begins by looking at the three states of matter before focusing on the gases. It reviews the gas laws of Boyle, Charles and Avogadro giving examples of how they are used in solving gas problems. The ideal gas equation is also discussed.

Rationale
Sound knowledge of the basic properties and the laws governing the behaviour of gases is necessary before tackling the learning material in Unit I. The kinetic molecular theory, which is the major focus of Unit I explains the behaviour of gases at a molecular level and justifies the gas laws.
XII. Compulsory Resources

Resource #1

**Complete reference : Chem1 Virtual Textbook**

http://www.chem1.com/acad/webtext/virtualtextbook.html

**Abstract**

The virtual textbook is an online chemistry book with a wide range of chemistry topics. The book can be viewed online and contains downloadable PDF files. It provides a reference text and is an alternative source for information for you. It makes use of illustrations that make for easier comprehension. The online version allows you the student to make a step-by-step progression as you study any of the available topics.

**Rationale**

This resource is essential reference material for a number of units in this module. In particular, properties of matter, chemical energetics and thermodynamics of chemical equilibrium are some of the chapters relevant to the study of this module. Examples are included in the textbook to provide insights into the application of the concepts, which you would have learnt.

Resource #2

**Complete reference :**

Chemistry Experiment Simulations and Conceptual Computer Animations

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/simDownload/index4.html#kinetics

**Abstract**

This site has animations and experiments illustrating various concepts found in this module. Simulations and demonstrations relevant to this module include those that relate to Boyle’s law, Charles’s law and effusion. Experiments involving gas properties and heat changes are also given.

**Rationale**

This resource provides simulated demonstrations and experiments to help you understand concepts of chemistry, which are sometimes difficult for the learner to visualise. Reading of the learning material in conjunction with these simulations will assist the learner in understanding the concepts.
XIII. Useful links

Useful links # 1

The catalyst: chemistry resources for teachers
http://www.thecatalyst.org

Description
The site targets secondary school chemistry education learners and provides an on-line resource for teaching chemistry. The Catalyst is a valuable web resource for finding information on various aspects of chemistry.

Rationale
This site is gateway to a number of resources. Links to specific topics in chemistry and those of a general nature are found on the website. Visitors to the site have an opportunity to make online submissions on various aspects in chemistry.

Useful link # 2

Science Resource Centre
http://chem.lapeer.org

This web site is for science teachers to share ideas. I would like to provide labs, demonstrations, and any other information which teachers can access. Permission is hereby granted to use and reproduce all materials at this site as long as the activities are not sold. Individual authors retain any and all copyrights. If you would like to contribute, please send me a copy of the document as an e-mail attachment. Select "Sending Files" under the Miscellaneous menu option.

Latest award this site has received: SCIlinks®
Description

A number of learning and teaching resources are available on the site. Several demonstration experiments and practical laboratory experiments for onsite activities are given. Teaching tips are also provided for some concepts that are generally found to be problematic to the learner and for the teacher to teach.

Rationale

The site is particularly useful for the chemistry teacher as it provides a wide range of tools for demonstrating various concepts in chemistry. Demonstrations of reactions involving gases and the effect of reaction surface area on the reaction rate are two examples. Several laboratory investigations are also available to download and be given to learners. This site also affords teachers a point for information exchange.

Useful Links # 3

Chemistry Teaching Web Sites

http://people.moreheadstate.edu/fs/h.hedgec/sciteach.html

Description

The website is essentially designed to provide useful information to the chemistry teacher. A number of useful links are available on the site including one for science libraries. Links for teachers to share ideas including laboratory information and demonstrations are also provided.

Rationale

This is a useful site for chemistry teachers and learners especially those who are not used to searching for information on the internet. It also provides several other helpful sites. A wide range of chemistry resources are accessible from this site.
Useful Link #4

Mitopencourseware

http://ocw.mit.edu

Description

The site presents an array of lecture materials for free downloading. Topics are organised in a sequential order which makes access to topics of interest much easier. Thermodynamics is well covered in lecture notes that are in PDF format. Some of the lecture notes are scanned handwritten notes as presented in a classroom environment, giving the reader a feeling of the real classroom.

Rationale

This website is essentially a collection of lectures. The materials are particularly useful for the topics in Units II and III. The materials found on this site maybe used as supplementary reading.

Useful Link #5

Chemical kinetics with wikipedia

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

Description

This is a free encyclopaedia and covers the basic aspects of chemical kinetics including rate laws and factors affecting rates of reaction. It contains links for accessing definitions and explanations of terms. The content is easy to read and gives a good overview of the topic.

Rationale

The site is ideal to read in preparation for Unit V or for quick revision of concepts covered in Unit V, such as factors affecting rates of reaction and the transition state theory. The learner may also access definitions and explanations on common terms used in the study of rates of reaction.
Useful link # 6

Chemistry Portfolio - Teaching and Learning

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

Description

This site provides several aspects of learning and teaching chemistry. Information from the site includes tips on how to establish learning goals and expectations for students, designing courses and syllabi. It is also useful for teachers wishing to up-date themselves with knowledge on how to improve students learning.

Rationale

Teachers are continuously looking into improving teaching and learning of chemistry. This site provides information that can make teachers more effective by providing latest information on teaching and learning. The learner may also benefit from the learning tips that are given.
Useful link # 8

Chemistry@davidson

http://www.chm.davidson.edu/ChemistryApplets/index.html

Description

This is a site rich with virtual experiments and demonstrations for a whole range of topics in chemistry. The site provides information necessary to run the simulations and also allows downloading of chemistry Applets which can be deployed on local systems. The topic layout is well presented making it easy for the learner to access the appropriate experiments for a particular learning activity.

Rationale

Several experiments related to learning activities in this module are available at this site such as chemical kinetics, kinetic molecular theory and calorimetry. The experiments are well tabulated with a brief concept and description of the activity given. The learner is encouraged to identify and attempt to perform experiments at the end of a learning activity. The exercise accompanying the experiments should assist in evaluating the student conceptual understanding of topics.
XIV. Learning Activities

Learning activity # 1

Title of Learning Activity:
Kinetic Molecular Theory

Specific Teaching and Learning Objectives

When you have completed this activity you should be able to

• Use the kinetic theory to explain pressure-volume relationships for a gas (Boyle’s law)
• Explain using the kinetic theory temperature-volume relationships for a gas (Charles’s law)
• Account for the rate at which molecules and energy migrate through gases
• Derive the basic equation for the kinetic molecular theory of gases,
  \[ P = \frac{1}{3} \frac{N}{V} mu^2 \]
• Explain deviations from ideal gas behaviour as is found in real gases

Summary of the learning activity

Many common substances that we encounter around us are gases such as the air that makes up the earth’s atmosphere. There are also many practical applications that involve the use of gaseous substances. For example, car and bicycle tyres are inflated by pumping in air. The goal of this module is to refine our understanding of the physical laws that govern the properties of gases. We shall use the kinetic molecular theory to account for these laws at molecular level. The kinetic theory helps us answer the question why

• the pressure of gas increases when the volume is decreased at constant temperature;
• the volume of a fixed amount of gas increases with increasing temperature;
• at a fixed temperature and pressure, the volume is directly proportional to the amount of gas;
• the pressure of a mixture of gases is the sum of the partial pressures of each gas in the mixture.
Key terms and concepts

- Absolute temperature ($T$)
- Atmospheric pressure
- Avogadro’s Law
- Boyle’s Law
- Charles’s and Gay-Lussac’s Law
- Dalton’s law.
- Distribution of molecular speeds
- Gas diffusion
- Gas random motion
- Kinetic energy
- Kinetic molecular theory
- Maxwell’s distribution
- Pressure of a gas ($P$)
- $PV = nRT$
- Root-mean-square speed
- Volume of a gas ($V$)

List of relevant readings

- Properties of Gases
- Gas laws

List of relevant resources

- Chem1 Virtual Textbook
  http://www.chem1.com/acad/webtext/virtualtextbook.html
- Chemistry Experiment Simulations and Conceptual Computer Animations
  http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/simDownload/index4.html#kinetics

Multimedia Resources

- Computer with internet connectivity to enable access to open source learning materials and interactive learning through email, video conferencing and use of CD-ROMs
- QuickTime Movie Player Software
- Shockwave Player Software
- Macromedia Flash Player Software
List of relevant useful links:

- The Catalyst: Chemistry Resources For Teachers
  http://www.thecatalyst.org
- Science Resource Centre
  http://chem.lapeer.org
- Chemistry Teaching Web Sites
  http://people.moreheadstate.edu/fs/h.hedgec/sciteach.html
- Mitopencourseware
  http://ocw.mit.edu
- Kinetic Theory Of Gases With Wikipedia

Detailed description of the activity

In this learning activity you will be introduced to the kinetic molecular theory of gases and will later use this theory to explain the behaviour of gases. By considering the various assumptions of the kinetic molecular theory you will provide a justification for Boyle’s, Charles’s, Dalton’s and Avogadro’s laws of gases. Calculation exercises will be used to illustrate application of the laws.

Formative evaluation

- As you go through this learning activity you will come across problems to test your conceptual understanding of the subject matter
- Rapid quizzes are provided to check your understanding
- Practical experiments will be given to evaluate your understanding of theory-practice relations
- Simulated pressure-volume-temperature experiments will be accompanied by individual exercises

Learning activities

Gaseous substances play important roles in many of our day-to-day activities, from life sustaining respiratory processes such as oxygen and nitrogen (animals and plants) to their use in safety devices such as air bags in motor vehicles. A good understanding of the properties of gases allows us to make safe use of various items containing harmful gaseous substances, for example handling of pressurized aerosol products and handling of gases that are asphyxiating.
Gases are observed to have the same type of behaviour or physical properties over a range of conditions in terms of pressure, temperature, and molar volumes. The gas laws or generalizations that you will study in this module are the product of countless experiments on the physical properties of gases that were carried out centuries ago. Each of these laws about the macroscopic behaviour of gaseous substances represents a milestone in the history of science. Together they have played a major role in the development of many ideas in chemistry. The gas laws help us to predict the behaviour of gases, but they do not explain what happens at the molecular level to cause or bring about the changes we observe in the macroscopic world. The relationship, however, between what happens at the sub-microscopic or molecular level and the macroscopic (physical) behaviour of substances has significance in several areas of chemistry.

The kinetic molecular theory of gases was developed by a number of physicists (James Clerk Maxwell and Ludwig Boltzmann) who found that the physical properties of gases could be explained or rationalised in terms of the motion of individual molecules. This molecular movement is a form of energy (kinetic energy to be precise) which is defined as the capacity to do work or to produce change.

**Kinetic molecular theory of gases**

Chiefly Rudolf Clausius (1822-1906), James Clerk Maxwell (1831-1879) and Ludwig Boltzmann (1844-1888) developed the kinetic molecular theory. Their theory is based on the following assumptions about the nature of gases at molecular level.

1. Molecules in a gas are in constant random motion and frequently collide with each other.

2. A gas consists of a large number of particles that are so small and separated by such large distances that their size is negligible. Attractive and repulsive forces between gas molecules are negligible.

3. Each molecule acts independent of the other molecules and is unaffected by their presence. At sufficiently low temperatures, all gases will condense into liquids suggesting the presence of intermolecular forces that become significant at low temperatures. Attractive forces are responsible for holding liquid and solid molecules together. The tendency for a gas to expand and fill the volume in which it occupies suggests the presence of negligible forces of attraction between molecules. Increasing pressure of a gas results in decrease of inter-particle distance and therefore more interaction between molecules.

4. Molecules collide with each other and the walls of the container. In these collisions, individual molecules may gain or lose energy. However, in a collection of molecules at constant temperature the total energy remains constant. The assumption is valid in the sense that if it were not true, then the pressure of a
gas would decrease gradually as it is a consequence of collisions with the wall of the container.

5. What about the average kinetic energy of the molecules which is proportional to the temperature of the gas in Kelvin? Any two gases at the same temperature will have the same average kinetic energy. This assumption enables us to write the equation that the average kinetic energy is proportional to the absolute temperature.

Application of the kinetic theory to the gas laws

On a qualitative basis, the kinetic theory of gases though simple can allow us to account for the general properties of gaseous substances as is illustrated in the sections that follow.

Boyle’s law

Boyle’s law gives the relationship between pressure and volume, if the temperature and amount are held constant. It states that for a fixed amount of gas at a constant temperature, gas volume is inversely proportional to gas pressure. How can we explain this law from a molecular viewpoint?

The pressure exerted by a gas arises from molecules impacting on the walls of the container. The number of collisions per unit time (second) is proportional to the density of the gas i.e. the number of particles per unit volume. It follows therefore that decreasing the volume results in increased density and therefore the collision rate. This shows that the pressure of a gas is inversely proportional to the volume it occupies. As the volume decreases, the pressure increases and vice-versa, \( P \propto \frac{1}{V} \).

Derivation of Boyle’s law

The mathematical statement of Boyle’s law maybe derived using the kinetic theory. The derivation starts by considering the fact that gas molecules are in constant random motion and continuously colliding with the walls of the container. Consider a molecule in a box, that under goes a collision with the walls in which it is contained.
Let us assume that the molecule has velocity with components $v_x$, $v_y$ and $v_z$ along the axes $x$, $y$ and $z$. If the molecules travels in a perpendicular direction toward the wall labelled ‘A’, it will have only one velocity component $v_x$. If the particle has mass, $m$, the momentum associated with this molecule will be

$$ P = mv_x \quad (1) $$

The molecule upon collision with the wall, its component of momentum along the axis similarly changes from $mv_x$ to $-mv_x$. The magnitude of the momentum remaining the same.

The number of collisions with the wall occurring in a time interval $\Delta t$ molecules is equal to the total number of molecules that reach the wall ‘A’ in that time interval. The distance a molecule with velocity $v_x$ can travel in time interval $\Delta t$ is $v_x \Delta t$.

Suppose all the molecules in a container have the same value of $v_x$, then all the molecules located within $v_x \Delta t$ will strike the wall, provided they are moving towards it. Figure 1 shows that all of these molecules within this region of the container will strike the wall within length $v_x \Delta t$ and cross-sectional area $A$.

If $N$ is the number of molecules per unit volume, the total number of molecules will be $N v_x \Delta t A$. On average, half the molecules will be moving towards the wall and the other half away from the wall. Therefore, the number of collisions that will occur at the wall in time $\Delta t$ is

$$ \text{Number of collisions} = \frac{1}{2} N v_x \Delta t A \quad (2) $$

The change in momentum in a single collision is $2mv_x$ and the total
\[ \Delta p = \frac{1}{2} N \nu_x \Delta t \text{A} A m \nu_x \]
\[ = N m A \nu_x^2 \Delta t \quad (3) \]

From classical physics, we know that the force exerted by an object is equal to the rate of change of momentum.

\[ F = \frac{\Delta p}{\Delta t} \quad (4) \]

1 Newton = 1 kg ms\(^{-2}\)

\[ F = N m A \nu_x^2 \quad (5) \]

Pressure is the force per unit area, in this case the area being \( A \). Therefore the pressure exerted on the wall is

\[ P = N m \nu_x^2 \quad (6) \]

Since the molecules in the gas are constantly changing speeds, the value of \( \nu_x^2 \) can be replaced with an average speed \( \langle \nu_x^2 \rangle \) giving

\[ P = N m \langle \nu_x^2 \rangle \quad (7) \]

As the molecules are in random motion, all directions are equivalent and the average \( \nu_x^2 \) is the same as the average in corresponding \( x \) and \( y \) directions

\[ \langle \nu_x^2 \rangle = \langle \nu_y^2 \rangle = \langle \nu_z^2 \rangle \quad (8) \]

Therefore, we can write the mean square speed as
Substituting in equation (7) we have

\[ \frac{1}{3} \rho = \frac{1}{3} \rho \frac{m}{3} \frac{N}{V} \left( \langle v \rangle \right)^2 \]  

(10)

We now replace the number of molecules, \( N \), by \( nN/V \) per unit volume where \( N \), is the number of molecules present and \( V \) is the volume of the container.

\[ P = nN_m \left( \langle v \rangle \right)^2 \]  

(11)

The product of \( m \) and \( N \) is the molar mass \( M \) so that equation (11) becomes

\[ P = \frac{1}{3} \frac{nM}{V} \left( \langle v \rangle \right)^2 \]  

(12)

This leads to the equation

\[ PV = \frac{1}{3} nM \left( \langle v \rangle \right)^2 \]  

(13)
Example 1

Consider a gas of 100 mL confined to a cylinder under a pressure of 1 atm. What would be the volume of the same gas at a pressure of 1.3 atm?

Solution

The problem involves pressure and volume at constant temperature. Boyle’s law can be used to solve the problem. Boyle’s law states that the pressure of a gas (P) is inversely proportional to the volume (V) for a given of gas at constant temperature.

\[ P \cdot V = k \]

where \( k \) is a constant.

Since \( P \cdot V = k \) is constant for a given system \( P_1 \cdot V_1 = P_2 \cdot V_2 \)

\[ V_2 = \frac{P_1 \cdot V_1}{P_2} \]

\( P_1 = 1 \text{ atm}, V_1 = 0.1 \text{ atm}, P_2 = 1.3 \text{ atm}, V_2 = ? \)

\[ V_2 = \frac{1 \text{ atm} \times 0.1 L}{1.3 \text{ atm}} = 0.0769 L \]

Practice problem 1

A gas bubble has a volume of 0.500 cm\(^3\) at the bottom of the lake where the pressure is 3.49 atm. What is the volume of the bubble at the surface of the lake where the pressure is 1 atm? Assume that the temperature is constant.

(a) 10 dm\(^3\) (b) 1.7 \times 10^3 \text{ dm}^3 (c) 1.7 dm\(^3\) (d) 1.7 cm\(^3\)
Interactive Exercise: **Boyle’s Law**

**Charles’s law**

The relationship between volume and temperature of a gas, if pressure and amount are held constant is given by Charles’s law. The law states that the volume of a fixed amount of gas at constant pressure is directly proportional to the absolute temperature. To explain this relationship we begin by looking at the relationship between the kinetic energy of the molecules and temperature of the gas.

The average kinetic energy of molecules is proportional to sample’s absolute temperature

\[
K.E = \frac{1}{2} mu^2 \quad (14)
\]

where \( m \) is the mass of the molecule and \( u \) is the speed of the molecule, \( \bar{u}^2 \), is the mean square speed of the molecules. From the preceding, we can write that

\[
K.E \propto T \quad (15)
\]

\[
\frac{1}{2} ma^2 \propto T \quad (16)
\]

where \( k \) is a constant and \( T \) is the absolute temperature. Raising the temperature increases the average kinetic energy of the molecules. This results in a higher frequency of collisions with walls of the container. In addition, the molecules will collide with greater impact with the walls. Since pressure is defined as the force per unit area, the pressure of the gas will increase with an increasing temperature. The gas will expand until the external pressure balances the gas pressure.

How fast does a molecule move, on the average, at any temperature \( T \)? One way to estimate molecular speed is to calculate the root-mean-square speed, which is an average molecular speed. One of the results of the kinetic theory of gases is that the total kinetic energy of the mole of any gas equals \( \frac{1}{2} kT \)

\[
\frac{1}{2} mv^2 = \frac{1}{2} RT \quad (17)
\]
where \( k \) is Boltzmann’s constant, of value \( 1.38 \times 10^{-23} \text{ J K}^{-1} \). The value of the product of the value of the Boltzmann’s constant and Avogadro’s number is the same as the gas constant \( R \).

\[
N_A \left( \frac{1}{2} \text{mv}^2 \right) = \frac{1}{2} RT
\]

where \( N_A \) is Avogadro’s number.

**Example 2**

A balloon is inflated to a volume of 2.5 L in a warm living room (24 °C). Then it is taken outside on a very cold winter’s day (–25 °C). Assume that the quantity of air in the balloon and its pressure both remain constant. What will be the volume of the balloon when it is taken outdoors?

**Solution**

The volume of a fixed amount of gas at constant pressure is directly proportional to the absolute temperature.

\[
V \propto T
\]

\[
V = kT
\]

\[
\frac{V}{T} = k
\]

where \( k \) is a constant.

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2} = k
\]

Solving for \( V_2 \) with temperature in Kelvin scale gives us

\[
V_2 = \frac{V_1 \times T_2}{T_1}
\]

\[
V_1 = 2.5 \text{ L}, \ T_1 = 297 \text{ K}, \ T_2 = 248 \text{ k}, \ V_2 = (?)
\]
Interactive Exercise: Charles’s Law

**Avogadro’s Law**

This law states that at a fixed temperature, the volume of gas is directly proportional to the amount of gas. If the number of moles of gas \( n \) is doubled, the volume doubles and so on. The mathematical statement is that \( V \propto n \) and \( V = kn \).

The pressure of a gas has been shown to be directly proportional to both density and temperature, while the mass is directly proportional to the number of moles. The density maybe represented by \( \frac{n}{V} \) and therefore

\[
P \propto \frac{n}{V} \tag{18}
\]

\[
P = C \frac{n}{V} T \tag{19}
\]

For two gases we can write

\[
P_1 = C \frac{n_1 T_1}{V_1} \tag{20}
\]

\[
P_2 = C \frac{n_2 T_2}{V_2} \tag{21}
\]

If the two gases were under the same conditions: pressure \( (P_1 = P_2) \), volume \( (V_1 = V_2) \) and temperature \( (T_1 = T_2) \), the \( n_1 \) is equal to \( n_2 \) which is Avogadro’s law.
Example 3

Cyclopropane (C₃H₆) is a gas used as an anaesthetic. What would be the mass of 1.0 L of the gas measured at standard temperature and pressure?

The law states that at a fixed temperature and pressure, the volume of a gas is directly proportional to the amount of gas. At STP 1 mol of gas = 22.4 L.

\[
\text{Mass gas} = 1.00 \text{ L} \times \frac{1 \text{ mol} \times 42.8 \text{ g mol}^{-1}}{22.4 \text{ L}} = 1.88 \text{ g}
\]

Practice problem 3

A car travelling at 16 km/h produces 150 g CO per kilometre. How many moles of CO are produced per kilometre?

(a) 5.4 (b) 3.4 (c) 5.0 (d) 53.6

Dalton’s law of partial pressures

Dalton’s law of partial pressures states that for a mixture of gases, the total pressure of the mixture is the sum of the partial pressures of the component gases of the mixture. This law is in effect evidence of one of the postulate of the kinetic theory. It has been assumed that molecules have negligible intermolecular forces. If each molecule acts independently, it then follows that the pressure exerted by one molecule is independent of the presence of another molecule. The total pressure therefore is given by the sum of individual gas pressures.

Example 4

The combustion of methane gas produces carbon dioxide and water. Calculate the partial pressure of the water vapour if the total pressure of the gaseous products is 6.25 torr.

Solution

The reaction is according to the following equation.

\[
\text{CH}_4 (g) + 2\text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2\text{H}_2\text{O} (g)
\]

According to Dalton’s law of partial pressures, the total pressure of a mixture of gases is the sum of their individual partial pressures.

\[
P_T = P_A + P_B + P_C + \ldots
\]

where \(P_i\) is the partial pressure of each gas in the mixture.
Partial pressure of each component is given by mole fraction of each component multiplied by the total pressure of the gas mixture. If \( P_{H_2O} \) is the partial pressure of water vapour, \( n_{H_2O} \) the number of moles of water produces and \( n_T \) the total numbers of moles produced, we can write the following expression taking into account the stoichiometry of the reaction.

\[
P_{H_2O} = \frac{n_{H_2O}}{n_T} \times P_T = \frac{2 \times 6.25 \text{torr}}{3} = 4.16 \text{torr}
\]

**Practice problem 4**

In an experiment a mixture of oxygen and nitrogen gas is collected over water at 30 °C and 700 torr pressure. What is the partial pressure of oxygen, if the partial pressure of nitrogen is 550 torr? (Vapour pressure H2O at 30 °C, 4.2455 kPa).

(a) 118 torr   (b) 120   (c) 115   (d) 119

**Distribution of molecular speeds**

Molecules in a gas are constantly undergoing random motion and collisions. Molecules change their speeds after each collision and as a result molecules will be moving with a range of speeds. Since the number of molecules is large we can use statistical methods to establish a distribution of their speeds. The distribution of molecular speeds is known as the Maxwell – Boltzmann distribution that is shown in the diagram below.

**FIGURE 2**

Diagram showing the different characteristics speeds for a sample of gas
Three characteristic speeds are shown in the diagram. More molecules have the speed \( u_m \), known as the most probable or modal speed, than the other two. The simple average speed is \( u_{av} \) whilst \( u_{rms} \) is the square root of the average of the squares of speeds of all molecules in a sample.

We can derive a useful equation for \( u_{rms} \). One of the results of the kinetic theory of gases is that the average kinetic energy of a gas is \( \frac{1}{2} kT \). From the preceding sections we noted that the average kinetic energy of a molecule is given by \( \frac{1}{2} m \bar{u}^2 \) so that for Avogadro number \( N_A \) we can write

\[
N_A \left( \frac{1}{2} m \bar{u}^2 \right) = \frac{1}{2} kT
\]

The equation maybe re-written to

\[
3RT = N_A m \bar{u}^2
\]

Note that the product \( N_A m \) represents the mass of 1 mole of molecules i.e. mass \( M \).

\[
3RT = M \bar{u}^2
\]

Solving for \( \bar{u}^2 \) and the taking the square root

\[
u_{rms} = \sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{M}}
\]

Maxwell analysed the behaviour of gases at different temperatures and the results are depicted in the figure below.
The peak of the most probable speed increases as temperature increases. Also, it flattens out increasing with increasing temperature.

**Example 5**

Calculate the root-mean-square speed in meters per second for Cl\(_2\)(g) molecules at 30 °C.

**Solution**

The expression for \(u_{\text{rms}}\) is used

\[
 u_{\text{rms}} = \sqrt{\frac{3RT}{M}}
\]

For chlorine \(M = 70.91 \text{ g} = 7.09 \times 10^{-4} \text{ kg}\), \(T = 303 \text{ K}\), \(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}\)

Substituting in the equation

\[
 u_{\text{rms}} = \sqrt{\frac{3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 303 \text{ K}}{7.09 \times 10^{-2} \text{ kg mol}^{-1}}} = 326 \text{ m s}^{-1}
\]

**Practice problem 5**

At what temperature would the \(u_{\text{rms}}\) for Ne (g) be expected to be the same as that for He (g) at 300 K?

(a) 1000   (b) 150   (c) 1500   (d) 1600
**Diffusion and effusion of gases**

Diffusion is the migration of molecules of different substances as a result of the random motion of molecules. Although gas molecules are consistently having collisions resulting in frequent changes in direction, the net rate at which a gas moves in a particular direction depends on the average speed. Diffusion always proceeds from a region of higher concentration to one of lower concentration.

**FIGURE 4**
Path travelled by a single gas molecule in which each change in direction represents a collision

Effusion is a process related to diffusion, it is the escape of gas molecules from their container through an orifice (pinhole). Consider the effusion of a mixture of gases through an orifice as shown in the figure below.

**FIGURE 5**
Path travelled by a single gas molecule in which each change in direction represents a collision

The rates at which the two effusion can be compared are given below.

\[
\frac{\text{Rate}_{\text{effusion of } A}}{\text{Rate}_{\text{effusion of } B}} = \frac{u_{\text{rms}}(A)}{u_{\text{rms}}(B)} = \sqrt{\frac{3RT}{M_A}} = \sqrt{\frac{M_B}{M_A}}.
\]

(26)

This result is a statement of Graham’s law, which states that the rate of effusion (or diffusion) of two different gases are inversely proportional to the square roots of their molar masses.
In considering the equation above it is evident that lighter gases will effuse faster than the heavier gases. The consequences of the above theory maybe summarised that ratios of the root-mean-square speeds are equal to the ratios of

- rates of effusion
- effusion times
- amount of gas effused
- distance travelled by the molecules
- amount of gas effused
- molecular speeds

**Interactive Exercise: Effusion**

**Example 6**

Calculate the ratio of the diffusion rate for H\textsubscript{2}O and D\textsubscript{2}O (D is deuterium an isotope of hydrogen).

Molar mass H\textsubscript{2}O = 18.01 g mol\textsuperscript{-1}, D\textsubscript{2}O = 19.01 g mol\textsuperscript{-1}

\[
\frac{\text{Rate of diffusion H}_2\text{O}}{\text{Rate of diffusion D}_2\text{O}} = \sqrt{\frac{M_{\text{H}_2\text{O}}}{M_{\text{D}_2\text{O}}}} = \sqrt{\frac{19.01 \text{ g mol}^{-1}}{18.01 \text{ g mol}^{-1}}} = 1.02
\]

**Practice problem 6**

Two gases, HBr and CH\textsubscript{4}, effuse through a small opening. HBr effuses through the opening at a rate of 4 cm\textsuperscript{3} s\textsuperscript{-1}, at what rate will the CH\textsubscript{4} molecules effuse through the same opening.

(a) 9 cm\textsuperscript{3} s\textsuperscript{-1} (b) 10 cm\textsuperscript{3} s\textsuperscript{-1} (c) 8.5 cm\textsuperscript{3} s\textsuperscript{-1} (d) 9 m\textsuperscript{3} s\textsuperscript{-1}
The ideal gas law

In the previous sections we have looked at three historical laws that relate to two physical properties keeping all other properties constant. These laws and their mathematical expressions are shown below:

- **Boyle’s law**: \( P \propto \frac{1}{V} \) where \( T \) and \( n \) are constant
- **Charles’s law**: \( V \propto T \) where \( P \) and \( n \) are constant
- **Avogadro’s law**: \( V \propto n \) where \( P \) and \( T \) are constant

The three gas laws can be combined to give a single general gas law

\[
\frac{PV}{T} \propto n \tag{27}
\]

We can replace the proportionality symbol \( \propto \) with an equal sign by introducing a proportionality constant. If the constant is given the symbol \( R \), then

\[
\frac{PV}{T} = nR \tag{28}
\]

\( R \) is called the universal gas constant. The value and units of \( R \) depend on the units that are used for pressure, volume, temperature, and number of moles. The equation can be rearranged to the expression

\[
P V = n R T \tag{29}
\]

called the **ideal gas equation**. An ideal gas is one whose behaviour can be accurately described by the ideal gas equation.
Example 7
How many moles of hydrogen are present in a 50 L vessel if the pressure is 10 atm and the temperature is 25 °C?

Solution
The volume, pressure and temperature are given. The ideal gas law relates all the quantities given.

$$PV = nRT$$

$$P = 10 \times 101325 \text{ Nm}^{-2} = 1.01 \times 10^6 \text{ Nm}^{-2}, \quad V = 50 \times 10 \text{ m}^3, \quad T = 298 \text{ K}, \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$n = \frac{50 \times 10^{-3} \text{ m}^3 \times 10 \text{ atm} \times 101325 \text{ Nm}^{-2}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$$= 20$$

Real gases: deviation from ideal gas

Real gases do not conform to ideal gas behaviour. A plot of $PV$ against pressure shows that whereas the $PV$ is constant for an ideal gas, this is not true for real gases.

Real gases do not follow the assumptions of the ideal gas behaviour. Deviations from ideal gas behaviour of varying degrees are seen when $PV$ is plotted against $P$. Gases with only weak intermolecular forces give straight lines at low pressure and are close to the ideal gas behaviour. Significant deviation is observed for gases with strong intermolecular forces such as oxygen and nitrogen. Another assumption made when dealing with ideal gases is that molecules have no volume whereas real gases have a defined volume.
The ideal gas equation has been modified with corrections so that it fits with experimental data corresponding to real gases. One such effort was made by van der Waals. The van der Waals equation is the form

\[
\left( P + \frac{n^2a}{V^2} \right)(V - nb) = nRT
\]  

(30)

where \(a\) and \(b\) are known as van der Waals constants. The constants are determined experimentally by measuring \(P\), \(V\) and \(T\) under a set of different conditions. Corrections are also made relating to the pressure and the fact that molecules of real gases have a definite volume. The correction \(\frac{n^2a}{V^2}\) is intended to bring the mean pressure to that of the ideal gas. The correction \(nb\) brings the volume of the gas to what the ideal gas volume would be.
Learning activity # 2

Title of Learning Activity: Thermodynamics

Specific Teaching and Learning Objectives

When you have completed this activity you should be able to

• Define the terms: system, surroundings, open system and closed systems
• Define, explain and distinguish the concepts of heat, work and energy both from a theoretical and experimental point of view
• Describe and explain the law of conservation of energy
• Differentiate between state functions and non state functions
• Define heat capacity and specific heat. Describe how these quantities can be measured experimentally
• Distinguish between enthalpy and thermal energy

Summary of the learning activity

Thermodynamics is concerned with the interconversion of thermal energy and other kinds of energy. Understanding the underlying principles provide us with useful guidelines for appreciating energy changes and predicting the direction of the process. This unit focuses on the first law of thermodynamics. Most common processes take place at either constant volume or pressure. After learning the first law, we shall then apply it to processes occurring at constant volume and constant pressure.

List of relevant readings

• Chemical Energetics
• Heat, Work And The First Law
• Isothermal Expansion Of A Gas
List of relevant resources

- **Chem1 Virtual Textbook**
  http://www.chem1.com/acad/webtext/virtualtextbook.html
- **Chemistry Experiment Simulations and Conceptual Computer Animations**
  http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/simDownload/index4.html#kinetics

Multimedia Resources:

- Computer with internet connectivity to enable access to open source learning materials and interactive learning through email, video conferencing and use of CD-ROMs
- QuickTime Movie Player Software
- Shockwave Player Software
- Macromedia Flash Player Software

List of relevant useful links

- **The Catalyst: Chemistry Resources For Teachers**
  http://www.thecatalyst.org
- **Science Resource Centre**
  http://chem.lapeer.org
- **Chemistry Teaching Web Sites**
  http://people.moreheadstate.edu/fs/h.hedgec/sciteach.html
- **Mitopencourseware**
  http://ocw.mit.edu

Detailed description of the activity

Thermodynamics allows chemists to predict whether a chemical process will occur under a given set of conditions. In this activity, the learner will be introduced to concepts of energy and its transformations into forms of work, heat and enthalpy. We will focus our attention particularly on pressure-volume work being the most common type of work encountered in chemical changes. The change of enthalpy (heat content) with temperature ($\Delta T$) known as heat capacity is also covered. In the various sections examples and practice problems are given to illustrate applications of specific concepts.
Formative evaluation

- As you go through this learning activity you will come across problems to test your conceptual understanding of the subject matter.
- Rapid quizzes are provided to check your understanding.
- Practical experiments will be given to evaluate your understanding of theory-practise relations

Learning activities

Key Concepts and Terms

- Adiabatic boundary
- Closed system
- Endothermic process
- Energy
- Exothermic process
- First law of thermodynamics
- Heat
- Heat capacity
- Internal energy
- Isolated system
- Isothermal process
- Kinetic energy
- Open system
- Potential energy
- Pressure-volume work
- Reversible process
- Specific heat
- State function
- Surroundings
- System
- Thermal energy
- Work

What is energy? The nature of energy

Energy is usually defined as the capacity to do work. Various processes in the body produce energy to operate the muscle and to maintain the body temperature. Energy is produced in some chemical processes whilst some chemical reactions require energy to take place.
Two basic forms of energy

There are two forms of energy: kinetic energy and potential energy.

**Kinetics Energy**

This energy is associated with motion of matter. A body of mass \( m \) moving with a velocity \( v \) will have a kinetic energy

\[
E_{K} = \frac{1}{2}mv^2
\]

A racing car, billiard balls or molecules in motion will have kinetic energy associated with them.

**Potential Energy**

Potential energy is the energy a body has by virtue of its position in a force field. Typical examples of force fields include gravitational, electrical and magnetic fields. Consider a body builder lifting dumbbells from the floor through a distance a distance \( h \) or a woman drawing water from well through a height \( h \). In both cases, the process involves moving objects of mass \( m \) against the force of gravity, \( g \), through a distance (in this case height) \( h \). The potential energy change involved in the two activities is given by \( mgh \) where \( g \) is a constant, the acceleration due to gravity.

Potential energy may also be associated with charged particles or species such as cations and anions and in chemical bonds.

**Practice problem 1**

Identify the various types of energy associated with different farming activities.

**Internal energy (\( E \))**

Internal energy represents the total energy of the system comprising two components: kinetic energy and potential energy. Kinetic energy is the energy associated with various types of molecular motion and movement of molecules. Potential energy arises from the attractive and repulsive forces within atoms or molecules. The internal energy from a chemistry point is the sum of the total kinetic and potential energy of the system.
Units of Energy

- From the expression of kinetic energy (Equation 1) it can be seen that energy has units of kg m$^2$ s$^{-2}$
  
  SI unit is Joule (J)
  
  $1\, J = 1\, \text{kg m}^2\,\text{s}^{-2}$
  
  Note that it is common to use kilojoules (kJ)

- Another unit of energy commonly used in nutrition is the calorie (cal). It is defined as the energy required to raise the temperature of 1 g of water by 1 °C.
  
  $1\, \text{cal} = 4.18\, \text{J}$
  
  The nutritional unit is kilocalories: $1\, \text{Cal} = 1000\, \text{Cal} = 4.184\, \text{kJ}$

Example 1

What is the kinetic energy of a truck carrying yams with a mass of 2000 kg travelling at 50 km/h?

Solution

\[
K.E = \frac{1}{2}mv^2
\]

\[
K.E = \frac{1}{2} \times 2000\, \text{kg} \times \left( \frac{50000\, \text{m}}{3600\, \text{s}} \right)^2
\]

\[
K.E = 193\, \text{kJ}
\]

Practice problem 1

How much potential energy does 1kg of water at the top of a waterfall that is 500 m deep possess? How much kinetic energy is converted in falling from the top to the base? Give the answer in joules and calories.
Thermodynamic systems and surroundings

The system is that part of the universe that we choose to focus on or study (in an experiment – a reaction flask) whilst the surroundings is everything else outside the system (area of focus). Three types of systems may be identified based on the exchange of matter and energy between the system and the surroundings.

In an open system, matter and energy can move through the boundary of the system and surroundings. For a closed system, energy can be absorbed or released but not mass through the boundary between the system and surroundings. Isolated systems do not allow neither energy nor matter to be transferred.

**FIGURE 1**
Different type of thermodynamic systems showing the types of energy and matter interactions with the surrounding.

- **Open system**
- **Closed system**
- **Isolated system**

**FIGURE 2**
Thermodynamic system.
Example 2

What type of system does a boiling kettle represent?

Solution

Both energy and matter can be transferred between a system and its surroundings. It is therefore an open system.

Practice problem 2

The vacuum flask is often used to illustrate one type of thermodynamics system. Which type is this?

(a) Open system  
(b) Closed system  
(c) Isolated system  
(d) Closed-isolated system

State functions and non-state functions

Thermodynamics is concerned with changes in the state of the system as defined by macroscopic parameters such as composition, volume, pressure, temperature and energy. These properties are said to be state functions. Such properties depend only on the initial and final states of the system and not on the path used to reach a certain condition. Work and heat on the other hand are examples of functions that depend on the route taken. Heat and work are therefore non-state functions.

Work, heat and energy

The term thermodynamics has its origins from studies involving heat, work and energy related to steam engines. In chemical thermodynamics, we study the role of energy in chemical change and in determining the direction of a reaction.

Work (w)

In simple language, work is said to have taken place when we do something. When an object is moved against an opposing force, work is done. Raising an object is an example of doing work. Chemical reactions do work when electrons are driven through a metal wire, eventually being used to drive a device, such as driving an electric motor. In chemistry, however, the most common work encountered is related to pressure-volume changes accompanying chemical reactions.

To illustrate the relationship between volume-pressure changes and work, consider the following system consisting of a piston. The system comprises a gas confined to a cylinder with a free moving piston. If one of the weights is taken off, the
piston will move so that the volume of the gas changes from an initial value, $V_1$, to a new value $V_2$.

Suppose that the object with mass $m_2$ is removed, the piston will move up through a distance ‘$h$’. Now, we previously defined pressure as the force per unit area.

$$P = \frac{F}{A} \quad (2)$$

This equation can be rearranged to express the force in terms of pressure and area.

$$F = P \times A \quad (3)$$

In classical mechanics work is the product of the force exerted on the body and the distance it is moved, that is

Work \((w)\) = force \((F)\) x distance \((h)\) = \(P \times A \times h\) \quad (4)

The product \(A \times h\) is effectively the change in volume, \(\Delta V\) and therefore \(w = P\Delta V\).

The example below is used to illustrate the application of the formula.
Example 3
A gas expands by 0.5 L against a constant pressure of 1 atm at 25 °C. How much work is done in joules by the system against the surroundings?

The work done is given by
\[ w = P\Delta V \]
\[ P = 1 \text{ atm}, \quad \Delta V = 0.5 \text{ L} \]
\[ = 101325 \text{ Nm}^2 \times 5 \times 10^{-4} \text{ m}^3 \]
\[ = 50.6 \text{ Nm} \]
\[ = 50.6 \text{ J} \]

Practice problem 3
A woman lifts a bag of charcoal weighing 25 kg to her head to carry. If she is 1.6 m tall how much work is done in lifting the bag from ground to her head?

(a) 390 (b) 392 J (c) 40 (d) 400

Heat (q)
When two bodies are in thermal contact, energy flows from the warmer body to the cooler one – thermal energy is transferred. The molecular explanation for this process is that the molecules are in constant random motion and have kinetic energy associated with them. When two objects are in contact, thermal energy is transferred until the average kinetic energy between the two bodies is the same (thermal equilibrium).

Chemical changes involve release or gain of heat from the system to the surroundings. An exothermic process is one that releases heat to the surroundings. For example, combustion reactions are exothermic whilst a process such as vaporisation of water is endothermic. Energy is absorbed by the system in an endothermic process.

Because energy cannot be created or destroyed, any energy lost by the system must be gained by the surroundings. Thus, the heat generated by the combustion process is transferred from the system to its surroundings. The reaction is an example of an exothermic process, which is any process that gives off heat, i.e. transfers thermal energy to surroundings.

\[ \text{CH}_4(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O} (g) \]

In an endothermic reaction or process heat is absorbed by the system from the surroundings, the temperature of the systems will thus tend to drop as the reaction proceeds. Thermal energy is transferred from the surroundings to the system in an endothermic reaction or process. For example, when \( \text{Ba(OH)}_2.8\text{H}_2\text{O} (s) \) and
NH₄Cl (s) are mixed at room temperature the temperature is seem to decrease during the reaction.

\[
\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} (s) + \text{NH}_4\text{Cl} (s) \rightarrow \text{BaCl}_2 \cdot 2\text{H}_2\text{O} (s) + 2\text{NH}_3 (aq) + 8\text{H}_2\text{O} (l)
\]

**Law of the conservation of energy**

The first law of thermodynamics is essentially a statement of the law of the conservation of energy. It states that energy can neither be created nor destroyed. It can only be redistributed or converted from one form to another. A useful way to express this in chemistry is through the equation

\[
\Delta E = q + w
\]

where \( q \) is the heat absorbed and \( w \) is the work done by the system. Although the internal energy cannot be directly measured, the two quantities heat and work are measurable quantities. If heat flows into the system (or the surroundings do work on the system), the internal energy of the system increases – the sign of \( w \) or \( q \) is positive. Conversely, if the heat flows out of the system or work is done by the system (at the expense of the system), the internal energy of the system will be negative.

**Volume-pressure work**

The work often encountered with chemical processes is that associated with the formation or disappearance of gaseous substances. This type of work is called pressure-volume work, expansion work or PV-work.
Expansion work

Consider the diagram below in which the external pressure is viewed as weights against the gas.

![Pressure-volume work diagram](image)

From classical physics, the work required to move an object through a distance $dx$ against an opposing force $F$ is

$$w = - F dx$$

where the negative sign is indicative that when the system does work against an opposing force, the internal energy of the system doing work will decrease. Recall that pressure is the force per unit area. Force therefore is the product of pressure and area. The work done when moving from state $A$ to $B$ is then expressed as

$$dw = - P_{ex} dV$$
Expansion against constant pressure

Consider the expansion of a gas confined in a cylinder as shown below.

The total work done in moving from an initial state 1 to 2 will involve a change in volume from \( V_1 \) to \( V_2 \) against a constant pressure \( P_{ex} \). We can then write that

\[
\mathcal{W} = - \int_{V_1}^{V_2} P_{ex} \, dV
\]

and since \( P_{ex} \) is constant

\[
\mathcal{W} = -P_{ex} \int_{V_1}^{V_2} \, dV
\]

The expansion from the initial state \((V_i)\) to final state \((V_f)\)

\[
\mathcal{W} = -P_{ex} (V_f - V_i) \quad \text{(if P is constant)}
\]

\[
\mathcal{W} = -P_{ex} \Delta V
\]

The area under the curve in Figure 6 represents the work done by the gas. A common example of this type of work is in an internal combustion engine of car where expanding gases are able to drive a piston. The lifting-off of rockets and space vehicles such as the space shuttle also involve expansion of gases.
Example 4

A hydrocarbon is burned in a container with a movable piston with a cross-section area of 0.5 m$^2$. If the piston moved a distance of 30 cm against a pressure of 1 atm, how much work is done in the expansion?

Solution

In expanding, the piston sweeps through a volume = cross section area x distance covered.

Change in volume $\Delta V = 0.5 \text{ m}^2 \times 0.3 \text{ m} = 0.15 \text{ m}^3$, $P = 1 \text{ atm} = 101325 \text{ Nm}^{-2}$

From equation (11), $w = -P \Delta V = -(101325 \text{ Nm}^{-2} \times 0.15 \text{ m}^3)$

$= -15199 \text{ J}$

$= -15.2 \text{ kJ}$

Practice problem 4

A sample of gas is compressed from an initial volume of 4.0 L to a final volume of 1.0 L. What is the work done if the external pressure is 5 atm?

(a) $5.0 \times 10^3$
(b) $1.8 \times 10^3$
(c) $1.5 \times 10^3$
(d) $1.6 \times 10^2$

Reversible expansion of a gas

Suppose that the gas expands or contracts in such way that the external pressure equals the pressure of the gas. Such expansion/compression is said to take place in a reversible manner. A reversible change is one that proceeds via an infinitesimal amount and maybe changed to proceed in the opposite direction by an infinitesimal opposite action.

Isothermal reversible expansion of a gas

The process described above could be done reversibly and under isothermal conditions (e.g. constant temperature water bath). Using the equation for an ideal case and equation (8), we can evaluate the work done during this process.

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$  \hspace{1cm} (12)
The above expression will be positive if the initial volume, $V_i$, is greater than the final volume, $V_f$, indicating a compression process. The work done during the process maybe drawn using an indicator diagram in Figure 7.

In comparing the two areas (a and b), it is clear that more work is done during a reversible expansion against a constant external pressure than during an irreversible expansion process. Maximum work is obtained during a reversible expansion because maximum work is ensured at every step – no wastage.

**Free expansion**

Free expansion involves expansion with no opposing force. For example if the gas were to expand into a vacuum. In such a case $P_{ex} = 0$, so that the work done is equal to zero ($dw = 0, w = 0$) i.e. no work is done during free expansion of a gas.

**Constant pressure and constant volume process**

These are the most common processes encountered in chemical reactions. It is thus instructive to consider the behaviour of the first law of thermodynamics in relation to such processes.

**Constant volume processes**

To carry out a reaction at constant volume we would need a sealed vessel to contain any gaseous products produced. Typical equipment used to perform such measurements is the bomb calorimeter, frequently used to carry out combustion reactions.
In the previous sections, we have seen that the change in internal energy \( E \) is given by

\[
\Delta E = q + w \quad (13)
\]

If work is done by the system then

\[
w = -P_e \Delta V \quad (14)
\]

Thus,

\[
\Delta E = q + (-P_e \Delta V)
\]

In this case, \( \Delta V \) is zero therefore

\[
\Delta E = q_v \quad (15)
\]

where \( q_v \) indicates that heat involved is at constant volume. The result is significant as it shows that the heat change at constant volume is equal to the change in internal energy of the system. Thus, we can experimentally determine the internal energy change for a reaction by measuring energy absorb or released in the process.

**Example 5**

An ideal monoatomic gas is expanded at 298 K from an initial pressure of 5 atm to a final pressure of 1 atm isothermally and reversibly. Calculate the heat absorbed by the gas (q), work done on the gas (w) and the change in internal energy (\( \Delta E \)).

**Solution**

Since the process is taking place isothermally and at constant pressure, \( T_1 = T_2 \), \( \Delta T = 0 \) and

\[\Delta E = 0.\]

For a reversible process, the work done by the gas expanding isothermally and reversibly equation (12) can be used where the inverse relationship of pressure and volume is utilised i.e.
From the first law of thermodynamics, $\Delta E = q + w$

But $\Delta E = 0$, therefore $q = -w$

$q = -w = 3990 \text{ J mol}^{-1}$

**Practice problem 5**

Find the work done on the surroundings when 12 litres of an ideal gas, initially at a pressure of 10 atm is allowed to expand at constant pressure to 10 litres: (a) by reducing the external pressure to 1 atm; (b) by reducing pressure first to 5 atm, and then 1 atm; (c) allowing gas to expand into an evacuated space so that its total volume is 10 litres.

**Heat capacity**

The heat capacity ($C$) measures the temperature change experienced by a substance as a result of heat flow. It is the amount of heat energy required to raise its temperature by 1 K (or °C), mathematically expressed as

$$C = \frac{dq}{dT}. \quad \text{(16)}$$

The heat capacity of 1 mol of a substance is called its *molar heat capacity* and the heat capacity of 1 gram of a substance is called its *specific heat*.

For a constant volume process, we can write the following expression for the heat capacity.

$$C_v = \frac{dq_v}{dT} = \frac{dE}{dT}. \quad \text{(17)}$$
Constant pressure processes: enthalpy of reactions

Most chemical reactions take place at constant pressure, for example in the laboratory at atmospheric pressure. In such processes, volume changes do occur.

\[ q_p = \Delta E + P \Delta V \] at constant pressure \hspace{1cm} (18)

Heat evolved or absorbed at constant pressure, \( q_p \), is known as enthalpy, symbolized by \( H \), \( q_p = \Delta H \). It follows that

\[ \Delta H = \Delta E + P \Delta V \] \hspace{1cm} (19)

The enthalpy is then the change in internal energy plus the pressure-volume work. If it is assumed that the gases produced in a reaction behave as ideal gases, we can solve for \( V \) using the perfect gas equation to give us

\[ V = \frac{nRT}{P} \] \hspace{1cm} (20)

For a change in volume we can write

\[ \Delta V = \Delta \left( \frac{nRT}{P} \right) \] \hspace{1cm} (21)

If the reaction is taking place at constant temperature and pressure

\[ \Delta V = \Delta n \left( \frac{RT}{P} \right) \] \hspace{1cm} (22)

The change in volume for the reaction is essentially a change in number of moles of the species involved. Substituting equation (22) in equation (19), the enthalpy expression becomes

\[ \Delta H = \Delta E + \Delta n_{\text{gas}} RT \] \hspace{1cm} (23)

where \( \Delta n_{\text{gas}} \) is given by \( \Delta n_{\text{gas}} = \sum n_{\text{gas, products}} - \sum n_{\text{gas, reactants}} \) and represents the change in number of moles between the reactants and products.
The heat capacity at constant pressure is expressed in the equation

\[ C_p = \frac{dq_{in}}{dT} = \frac{dH}{dT} \]  \hspace{1cm} (24)

**Example 6**

Carbon monoxide poisoning sometimes occurs during the cold season due to indoor use of charcoal braziers for heating. This occurs when the amount of oxygen is limited. With sufficient air (oxygen) the carbon monoxide reacts with oxygen to form carbon dioxide which is somewhat less harmful. Calculate \( \Delta H \) for the reaction at 25 °C given that the change in internal energy for the reaction is - 281.7 kJ.

**Solutions**

\[ \text{CO (g)} + \frac{1}{2} \text{O (g)} \rightarrow \text{CO}_2 (g) \hspace{1cm} \Delta E = -281.7 \text{ kJ} \]

The enthalpy change enthalpy, \( \Delta H \), is defined as the sum of the change in internal energy, \( \Delta E \), and the pressure-volume work done by the system.

\[ \Delta H = \Delta E + P \Delta V \]

Since there is no indication of pressure and volume an alternative method is used to workout the problem as shown in equation (23).

\[ \Delta H = \Delta E + \Delta n_{\text{gas}} RT \]

\[ \Delta n_{\text{gas}} = 1 \text{ mol CO}_2 - (1 \text{ mol C0} + 0.5 \text{ mol O}_2) = -0.5, \Delta E = -281.7 \text{ kJ}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T = 298 \text{ K} \]

Substituting the equation (23)

\[ \Delta H = -2.817 \times 10^5 \text{ J} + (-0.5 \text{ mol x 8.314 J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) \]
\[ = -2.817 \times 10^5 - 1.238 \times 10^3 \]
\[ = -282.9 \text{ kJ} \]
Practice problem 6
One mole of methane reacted with oxygen at constant volume and at 298 K temperature according to the equation below.
\[ CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (l) \]
What is the change in enthalpy, \( \Delta H \), for the reaction if 886 kJ of energy is liberated during the reaction?
(a) - 881 kJ
(b) - 891 kJ
(c) 891 kJ
(d) - 886 kJ

Temperature dependence of reaction enthalpy
Not all reactions take place at 298 K, so we must examine how the tabulated thermochemical data can be adapted for use under different conditions. We have seen before that the heat capacity at constant pressure is related to temperature by
\[ \Delta H = C_p \, dT \]  \hspace{1cm} (25)
If a substance is heated from an initial temperature \( T_1 \) to a temperature \( T_2 \), the enthalpy change from \( H(T_1) \) to \( H(T_2) \) is according to the equation.
\[ H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \, dT \] \hspace{1cm} (26)
It is assumed that no phase transition occurred between the two temperatures of interests \( T_1 \) and \( T_2 \). For a chemical reaction equation (21) is expressed as
\[ \Delta H \text{rxn}(T_2) = \Delta H \text{rxn}(T_1) + \int_{T_1}^{T_2} \Delta H \text{rxn} \, C_p \, dT \] \hspace{1cm} (27)
where \( \Delta H \text{rxn} \) represents the standard enthalpies of reaction. This equation is known as Kirchoff’s law.

Interactive Exercise: Heat of Solution
Learning activity # 3

Title of Learning Activity: Thermochemistry

Specific Teaching and Learning Objectives

When you have completed this activity you should be able to

- Explain that chemical changes are accompanied by energy changes principally in the form of thermal energy
- Use the concept of enthalpy to explain endothermic and exothermic reactions
- Describe how changes in enthalpy and thermal energy accompanying a chemical reaction can be measured calorimetrically.
- Define bond energy. Use tables of bond energies to estimate the enthalpy of a reaction.
- Write and manipulate thermochemical equations
  - Combine a set of steps of thermochemical equations to obtain a net thermochemical equation (Hess's Law)
  - Write thermochemical equations for combustion and formation reactions

Summary of the learning activity

Thermochemistry is the study of thermal energy changes that accompany chemical changes. Combustion of fuels such as petrol used to drive cars and batteries used to power various electronic devices require some form of energy. Energy used in many applications involves chemical reactions before it is available to its intended purpose. In thermochemistry, we make use of heat changes to determine other thermodynamic properties: internal energy, enthalpy and heat capacity. Relationships established in thermochemistry allow computation of heat changes that are either too difficult or impossible to measure experimentally. This is done using tabulated thermochemical data.

List of relevant readings

- Chemical Energetics
- Thermochemistry
List of relevant resources

• Chem1 Virtual Textbook
  http://www.chem1.com/acad/webtext/virtualtextbook.html
• Chemistry Experiment Simulations and Conceptual Computer Animations
  http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/simDownload/index4.html#kinetics

Multimedia Resources

• Computer with internet connectivity to enable access to open source learning materials and interactive learning through email, video conferencing and use of CD-ROMs
• QuickTime Movie Player Software
• Shockwave Player Software
• Macromedia Flash Player Software

List of relevant useful links

• The Catalyst: Chemistry Resources For Teachers
  http://www.thecatalyst.org
• Science Resource Centre
  http://chem.lapeer.org
• Chemistry Teaching Web Sites
  http://people.moreheadstate.edu/fs/h.hedgec/sciteach.html
• Mitopencourseware
  http://ocw.mit.edu

Detailed description of the activity

This activity examines the changes in energy that accompany chemical transformations in chemical reactions. The change in enthalpy, a determining factor as to whether a reaction absorbs or releases heat, heat measurements involving calorimetry, and the application of Hess’s law to thermochemical problems and calculations are covered in this learning activity. Examples and chemical tasks to test your understanding of the topics covered are given throughout the text.
Formative evaluation

As you go through this learning activity you will come across

- problems to test your conceptual understanding of the subject matter.
- Rapid quizzes are provided to check your understanding.
- Experiments will be given to evaluate your understanding of theory-practice relations.
- Simulated experiments involving heat change accompanied with exercises.

Key Terms and Concepts

- Thermal energy
- Endothermic reaction
- Exothermic reaction
- Enthalpy
- Enthalpy change
- Enthalpy diagram
- Heat capacity
- Heat of reaction
- Hess’s law
- Standard enthalpy of formation
- Standard enthalpy of reaction

Learning activities

Many chemical reactions involve either evolution or absorption of heat. In the combustion of a common hydrocarbon fuel, for example petrol, air (oxygen) reacts to produce carbon dioxide in a process that involves bond breaking, rearrangement, and bond formation. Thermochemistry is concerned with heat exchanges following transformations such as chemical reactions and phase change. It enables us carry out calculations related to heat capacity, combustion and formation of various substances. Heat flow between the system and surroundings is easily measured and can be predicted from the enthalpies of the products and reactants.

Lowering of energy of a system

Systems that are unstable (high potential energy) have a higher tendency to undergo chemical change than systems that are stable (lower potential energy). Chemical reactions whenever possible tend to spontaneously move from a state of higher potential energy to one of lower potential energy. This is similar or akin to what would happen to a drum or cart perched at the top of the hill! It will
roll down. Take for example the combustion of charcoal, a common fuel used in most rural Africa for cooking and heating. The diagram in Figure 1 shows the change in energy when coal reacts with oxygen in air. The products are at lower energy than the reactants.

**FIGURE 1**
Energy diagram for the combustion of charcoal, a common household fuel in Africa.
**Enthalpy of reaction**

Chemical reactions involve either release or absorption of heat from the surroundings.

- When a chemical reaction occurs in which the system absorbs heat, the process is **endothermic** (it feels cold).
- When a chemical reaction occurs in which the system produces heat it is **exothermic** (it feels hot).

The heat of reaction is the quantity of heat exchanged between the system and its surroundings when chemical reactions occur. Heat will tend to flow until the system and surroundings are at the same temperature.

**FIGURE 2**

Diagram showing a reactions taking place in an open beaker. System in relations to its surroundings.

**Enthalpy**

Many chemical and biological processes take place at constant pressure. The heat released under conditions of constant pressure is a thermodynamic function known as enthalpy \( (H) \), sometimes referred to as “heat content.” The change in enthalpy (described or labelled as \( \Delta H \)) is not measured directly but through the energy released as heat. The enthalpy change (\( \Delta H \)) depends only on the initial and final states i.e.

\[
\Delta H = H_f - H_i
\]

Whether a reaction is exothermic or endothermic depends on the initial and final enthalpies of the reactants and products respectively.

- For **endothermic** reactions \( H_{\text{final}} > H_{\text{initial}} \) and \( \Delta H \) is positive (+\( \Delta H \))
- For **exothermic** reactions \( H_{\text{final}} < H_{\text{initial}} \) and \( \Delta H \) is negative (- \( \Delta H \))

The diagram in Figure 3 summaries exothermic and endothermic reactions. The diagram shows that for exothermic reactions, the products are lower in energy than the reactants whilst in endothermic reaction the energy of the products is higher than that of the reactants. The increase in enthalpy and extent of reaction are depicted on the y and x axes respectively.
When chemical reactions take place, either exothermic or endothermic, the principle of conservation of energy applies in relation to the system and surroundings. In an exothermic reaction heat flows from the system into the surroundings. The energy of the system must therefore decrease due to this loss whilst that of the surroundings increases due to the gain. In an endothermic reaction heat flows from the surroundings into the system so that the energy of the system increases. The energy of the surroundings decreases in the process.

Note that the products have lower energy (enthalpy) than the reactants in an exothermic reaction.
What are the properties of enthalpy as a state function?

- A property that depends only its initial and final state is known as a state function. The oxidation of sugar (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}) helps to illustrate the property of a state function. When eaten the body metabolises the sugar in the body to produce carbon dioxide and water.

\[
\text{sugar} - \text{carbon dioxide} + \text{water} + \text{energy}
\]

- In a different process of combustion, it will combine with oxygen, burns, to form the same products.

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + \text{O}_2(g) \rightarrow 12\text{CO}_2(g) + \text{H}_2\text{O(g)} + \text{energy}
\]

- Despite these two pathways, the overall change in enthalpy is the same since enthalpy is a state function.
- The enthalpy depends on the amount of substances reacting. Its magnitude depends on the amounts of reactants that are consumed.
- Reversing thermochemical equations also results in reverse of enthalpy sign but with the same magnitude
- Enthalpy change is also dependent on the state of the reactants and products i.e. must be specified.

How are enthalpy changes measured?

Experimental determination of heat evolved or released during chemical reactions is done using a calorimeter by measuring the temperature changes produced. If the calorimeter was isolated from the surroundings, the heat evolved in the reaction will be reflected in a rise in temperature of the system. The amount of heat evolved during the reaction can be determined from knowledge of how much energy is required to raise the temperature of a substance.

Heat capacity

- The heat capacity of an object is defined as the amount of heat energy required to raise its temperature by 1 K (or °C)
- The greater the heat capacity of an object, the more heat energy is required to raise the temperature of the object

For pure substances the heat capacity is usually given for a specified amount of the substance.
- The heat capacity of 1 mol of a substance is called its molar heat capacity
- The heat capacity of 1 gram of a substance is called its specific heat

The specific heat of a substance can be determined experimentally by measuring the temperature change (\(\Delta T\)) of a known mass (\(m\)) of the substance when it gains or loses a specific amount of heat (\(q\)):
The measurement of heat flow \((q)\) is known as calorimetry. Two types of calorimeters are described in the sections that follow.

**Constant pressure calorimeter**

In a constant pressure calorimeter, heat measurement is done under constant pressure conditions. The general construction of constant pressure calorimeter is shown below.

![Diagram of constant pressure calorimeter](image)

The calorimeter incorporates a pressure regulator to control the pressure. For reactions taking place at atmospheric pressure, the regulator is left open so that internal pressure equals external pressure.

Heat released or absorbed in the reaction will be reflected in the change in temperature. If heat is evolved for example, the solution will absorb the heat so that

\[ q_{\text{aq solvent}} = q_{\text{rxn}} \]
Constant volume calorimetry

In a constant volume calorimeter measurements are done at a fixed volume in a sealed container. The reaction is triggered in a chamber and the heat released is absorbed by the water surrounding the chamber. The constant volume calorimeter is ideal for measuring heats of reaction from combustion processes that involve the release of gases. In this setup (see Figure 6), all gases produced are contained within the vessel.

To carry out a determination, the bomb is assembled and filled with oxygen at high pressure. It is then immersed in water in the calorimeter and its initial temperature taken. The reaction is triggered by a short pulse of electricity, which heats the sample to a point of ignition. The change in temperature is monitored using a thermometer and the final temperature determined after the combustion.

Constant volume measurements allow us to determine the change in internal energy, $\Delta E$. From the first law of thermodynamics

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

If there is no change in volume then $P\Delta V = 0$ and hence $\Delta E = q$.

**Example 1**

Calculate the amount of heat required to raise the temperature of 9.25 L of water from 22.0 to 29.4 °C given that the specific heat of water is 4.18 J g$^{-1}$ °C$^{-1}$.

**Solution**

From equation (2)
Solving for the quantity of heat transferred \( q = \text{mass} \times \text{change in temperature} \times \text{specific heat of water}. \)

\[
q = 9.25 \times 10^3 \text{ g} \times (29.4 - 22.0) \degree \text{C} \times 4.18 \text{ J g}^{-1} \degree \text{C}^{-1}
\]

\[= 286.3 \text{ kJ}\]

**Practice problem**

A sample of carbon, 3.0 g, was burned to carbon dioxide in a copper calorimeter. The mass of the calorimeter was 1.5 kg and the mass of water in the calorimeter was 2 kg. The initial temperature was 20 \degree \text{C} and the final temperature was 31 \degree \text{C}. Calculate the heat liberated for the combustion of 1 g of carbon. The specific heat capacity or copper and water are 0.389 J g\(^{-1}\) \degree \text{C}^{-1} and 4.18 J g\(^{-1}\) \degree \text{C}^{-1}.

(a) 3.2 \times 10^4 \text{ J}
(b) 9.3 \times 10^4 \text{ J}
(c) 6.4 \times 10^4 \text{ J}
(d) 9.2 \times 10^4 \text{ J}

**Interactive Exercise:** _Calorimetry_

**Hess’s law**

Hess’s law states that when a reaction takes place to form products, the change in enthalpy is the same regardless of whether it is in a single step or involves several stages. For example, in the hypothetical reaction below.
The overall enthalpy change is given by

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

The significance of the law is that it enables calculation of enthalpies for reactions that may be difficult or too dangerous for us to perform in the laboratory. Many thermochemical data can be found in Tables for use in calculations for various chemical reactions.

**Standard enthalpy changes**

One restriction of Hess’s law is that all the enthalpies must be measured at the same temperature and pressure. Chemists generally perform experiments (chemical reactions) under a variety of conditions. It was therefore found convenient to measure and report enthalpy changes under an agreed set of standard conditions. All enthalpy changes measured under these conditions are referred to as standard enthalpy changes denoted by $\Delta H^\circ$. The reactant and products must be in their standard states. The standard state of a pure substance being the form (gas, liquid or solid) in which a substance is most stable at 1 atm pressure and a specified temperature.

**Standard enthalpy of reaction**

The standard enthalpy of reaction is the change in enthalpy during a chemical reaction. It is the difference between the enthalpies of the reactants and products. Take for example the hypothetical reaction below.

$$aA + bB \rightarrow cC + dD$$

The enthalpy change for this reaction maybe calculated from

$$\Delta H = \text{Sum of enthalpies of products} - \text{Sum of enthalpies of reactants}$$

Mathematically written as

$$\Delta H^\circ_R = ch^\circ_m(C) + dh^\circ_m(D) - ah^\circ_m(A) - bh^\circ_m(B).$$

**Example 2**

Phosphine gas may be prepared using by the following reaction.

$$Ca_3P_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(s) + 2PH_3(g)$$
Use the standard enthalpies of formation given below to calculate the standard enthalpy change for the above reaction.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_f^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ca}_3\text{P}_2$ (s)</td>
<td>-504</td>
</tr>
<tr>
<td>$\text{Ca(OH)}_2$(s)</td>
<td>-986</td>
</tr>
<tr>
<td>$\text{PH}_3$ (g)</td>
<td>+90</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$ (l)</td>
<td>-286</td>
</tr>
</tbody>
</table>

**Solution**

The enthalpy change for the reaction is given by the following relationship.

$$\Delta H = \text{Sum of enthalpies of products} - \text{Sum of enthalpies of reactants}$$

$$\Delta H = [3 \times (-986) + (3 \times 90)] - [(-504) + 6 \times (-286)]$$

$$= (-3048 + 270 + 504 + 1716) \text{kJ}$$

$$= 558 \text{kJ}$$

**Practice problem 2**

The enthalpy change for the combustion of 1 mole of pentane to carbon dioxide and water is -3526 kJ. Calculate the standard enthalpy of formation of pentane given the following standard enthalpies of formation.

- $\Delta H_f^\circ$ (CO$_2$ (g)) = -393 kJ mol$^{-1}$
- $\Delta H_f^\circ$ (H$_2$O (l)) = -286 kJ mol$^{-1}$

(a) -160 kJ
(b) 155.2 kJ
(c) -155.2 kJ
(d) -77.6 kJ

**Thermochemical calculations**

A thermochemical equation is a balanced reaction equation accompanied with the enthalpy change associated with it.

$$\text{Zn(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{ZnO(s)} + \text{H}_2\text{(g)} \quad \Delta H_f^\circ = -192.8 \text{kJ mol}^{-1}$$

From the preceding sections, the heat evolved or absorbed during a chemical reaction is the enthalpy change. In chemistry we normally do our experiments at standard conditions of temperature and pressure (STP). It is for this reason that results from thermochemical measurements are usually at STP.
Bond enthalpy and mean bond enthalpy

Bond dissociation enthalpy relates to enthalpy changes during formation and breaking of chemical bonds. Breaking of bonds requires an input of energy (endothermic) whilst formation of bonds gives off energy (exothermic). Bond dissociation energy is defined as the amount of energy required to break one mole of covalent bonds in gaseous species. Knowledge of how much energy is required in breaking and formation of new bonds in a chemical reaction provides us with information as to what type of energy change is likely for that particular reaction.

Reported bond dissociation enthalpies are average values for the bonds in a molecule. Typical average bond energies for selected molecules are shown in the Table below.

<table>
<thead>
<tr>
<th>Type of Bond</th>
<th>$\Delta H_d^\circ$/kJ mol$^{-1}$</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>N - H</td>
<td>389</td>
<td>NH$_3$, ammonia</td>
</tr>
<tr>
<td>O - H</td>
<td>464</td>
<td>H$_2$O, water</td>
</tr>
<tr>
<td>C - H</td>
<td>413</td>
<td>Average of many organic compounds</td>
</tr>
<tr>
<td>C - C</td>
<td>346</td>
<td>Average of many organic compounds</td>
</tr>
<tr>
<td>C - F</td>
<td>485</td>
<td>CF$_4$, carbon tetrafluoride</td>
</tr>
</tbody>
</table>

Mean bond enthalpy

Consider the combustion of methane to give carbon dioxide and water as the products.

$$\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 \quad +1646 \text{ kJ mol}^{-1}$$

The total enthalpy change involved in the above reaction is $+1646$ kJ mol$^{-1}$, this is the energy needed to break four C–H bonds. Therefore, the energy required to break one C–H is $+1646/4$ kJ mol$^{-1}$. It is necessary to use mean values because in breaking the covalent bonds successive dissociations differ. For example,

$$\text{CH}_4(g) \rightarrow \text{CH}_3(g) + \text{H}(g) \quad \Delta H_d^\circ = +427 \text{ kJ mol}^{-1}$$

$$\text{CH}_3(g) \rightarrow \text{CH}_2(g) + \text{H}(g) \quad \Delta H_d^\circ = +371 \text{ kJ mol}^{-1}$$

The energy released in a chemical reaction is the difference in the energy required to break bonds and that given out in the formation of new bonds. It is summarised as

$$\Delta H_{\text{rxn}} = \sum \text{BE (reactants)} - \sum \text{BE (products)} \quad (5)$$
Practice problem

Given the following thermochemical equations

\[
\begin{align*}
\text{BCl}_3 (g) + 3\text{H}_2\text{O} (l) & \rightarrow \text{H}_3\text{BO}_3 (g) + 3\text{HCl} (g) & \Delta H^\circ &= -112.5 \text{ kJ} \\
\text{B}_2\text{H}_6 (g) + 6\text{H}_2\text{O} (g) & \rightarrow 2\text{H}_3\text{BO}_3 (s) + 6\text{H}_2 (g) & \Delta H^\circ &= +493.4 \text{ kJ} \\
\text{H}_2 (g) + \text{Cl}_2 (g) & \rightarrow 2\text{HCl} (g) & \Delta H^\circ &= -184.6 \text{ kJ}
\end{align*}
\]

Calculate the value of \( \Delta H^\circ \) for the reaction

\[
\text{B}_2\text{H}_6 (g) + 6\text{Cl}_2 (g) \rightarrow 2\text{BCl}_3 (g) + 6\text{HCl} (g)
\]

(a) 492.2 kJ  
(b) 389.2 kJ  
(c) 3892 kJ  
(d) -389.2 kJ
Learning activity # 4

Title of Learning Activity: Spontaneity in Chemical Change

Specific Teaching and Learning Objectives

When you have completed this activity you should be able to

- Explain what is meant by a spontaneous process
- Define and explain the term entropy
- Explain the second law of thermodynamics
- Make qualitative prediction of the direction of a reaction based on entropy
- Define the term free energy and explain how it is related to equilibrium properties

Summary of the learning activity

This activity examines the origin of spontaneous changes in physical and chemical processes. Many natural processes are spontaneous processes. Examples include the dissolution of sugar in a cup of coffee, melting of ice or the rusting of iron. Common to all these processes is an increase in the degree of disorder. We shall introduce the concept of entropy to define, measure and discuss spontaneous processes. The second law of thermodynamics provides a basic criterion for spontaneous change. In discussing entropy, we need to look at both the system and surroundings. In chemical processes, our focus tends to be on the system. The use of the function free energy is discussed as the measure of spontaneity.

Key concepts and terms

- Absolute entropy
- Entropy and equilibrium
- Entropy, symbolized $S$
- Free energy and equilibrium
- Gibbs free energy
- Second law of thermodynamics
- Spontaneity
- Standard entropy change, symbolized $\Delta S^\circ$
- Standard free energy change, symbolized $\Delta G^\circ$
- Thermodynamic equilibrium constants
- Third law of thermodynamics
List of relevant readings

- Thermodynamic Equilibrium
- Criteria For Spontaneous Change
- Absolute Entropies

List of relevant resources

- Chem1 Virtual Textbook
- Chemistry Experiment Simulations and Conceptual Computer Animations

Multimedia Resources

- Computer with internet connectivity to enable access to open source learning materials and interactive learning through email, video conferencing and use of CD-ROMs
- QuickTime Movie Player Software
- Shockwave Player Software
- Macromedia Flash Player Software

List of relevant useful links

- The Catalyst: Chemistry Resources For Teachers
  [http://www.thecatalyst.org](http://www.thecatalyst.org)
- Science Resource Centre
  [Http://chem.lapeer.org](Http://chem.lapeer.org)
- Chemistry Teaching Web Sites
  [http://people.moreheadstate.edu/fs/h.hedgec/sciteach.html](http://people.moreheadstate.edu/fs/h.hedgec/sciteach.html)
- Mitopencourseware
  [http://ocw.mit.edu](http://ocw.mit.edu)

Detailed description of the activity

In this activity, we consider the question why does a reaction proceed as written in a chemical statement? How far does the reaction go? What factors favour spontaneous reactions in a chemical process? How much energy must be supplied to drive a particular reaction in the desired direction? The answers to these
questions are provided in this Unit. The Unit starts by looking qualitatively at what makes a reaction process spontaneous. A linkage between spontaneity and disorder is established leading to the statement of the second law of thermodynamics. Quantitative and qualitative measurement of this notion of disorder, is discussed by introducing a thermodynamic function known as entropy. Gibbs free energy, which combines the enthalpy change (you learned in Unit II) and entropy, is identified as a criterion for spontaneous chemical reactions or change.

**Formative evaluation**

- As you go through this learning activity you will come across problems to test your conceptual understanding of the subject matter.
- Rapid quizzes are provided to check your understanding.
- Practical experiments will be given to evaluate your understanding of theory-practise relations
- Simulated experiments accompanied with exercise are given in the activity.

**Learning activities**

The world is characterised by natural occurring processes that take place spontaneously. We observe spontaneous physical and chemical processes every day including many of the following examples. A waterfall runs downhill, but never up spontaneously. Ice if left to stand melts with no necessary action required for the process to continue. Sugar cubes spontaneously dissolve in a cup of coffee but dissolved sugar does not spontaneously reappear in its original form. Air released from a balloon comes out spontaneously. The reverse process that is the gathering of all the molecules into the balloon is not spontaneous. A beer glass that drops to the floor breaks into pieces, the reverse process does not happen spontaneously. In all these cases, the reverse process is non-spontaneous. These examples show that processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the opposite direction.

A spontaneous reaction does not necessarily mean an instantaneous reaction. Some reaction may occur instantaneously and rapidly (for example, explosives and fireworks) while other reactions such as corrosion occur at a very slow rate.

The second question that needs to be answered is why some reactions are favoured under one set of conditions and not others. For example, one of the greenhouse gases, nitrogen dioxide, produced in the reaction between nitrogen and oxygen is unfavourable at normal temperature. However, in an internal combustion engine of a car the high temperatures encountered make the reaction highly favourable.
What is the criterion for spontaneous change?

For common natural processes such as rolling down of a drum down a hill or water falling down the Victoria Falls, the common feature is the change in potential energy. The spontaneous change in the position of water or the drum in the examples above would suggest that the lowering in energy is the driving force for the spontaneous process. For chemical systems this is analogous to a change in the internal energy of the system, as in an exothermic chemical change. When heat is released from the system to the surroundings during a chemical reaction, the energy of the system decreases. The system energy changes from a higher state to a lower one. The analogue of the previous examples leads to the proposition that exothermic processes have a tendency to proceed spontaneously. Exothermic processes are generally spontaneous. Several endothermic processes are spontaneous. Typical examples include

- the melting of ice in which heat is absorbed and the energy of the system increases
- evaporation of water from a surface is also endothermic
- and so is the expansion of carbon dioxide into a vacuum

Conclusion – the enthalpy change alone is not sufficient to determine whether a change is spontaneous or not.

A spontaneous process is a process that occurs in a system such that left to itself requires no external intervention to continue. A non-spontaneous process is process that requires external action to start. A reaction that does occur under the given set of conditions is called a spontaneous reaction. If a reaction does not occur under specified conditions, it is said to be non-spontaneous

Spontaneity and disorder

All the examples that we have considered for spontaneous processes are characterised by a change to a more disordered state. In other words, there is an increase in the degree of randomness. In addition, there is no change in energy involved in the process. This point is illustrated further in the experiments described in the next sections.
Mixing of two gases

Two ideal gases are confined to two chambers separated by a valve as shown in the diagram below.

When the tap is opened, the gases migrate into opposite chambers and mix. Mixing continues until the partial pressures in each chamber are uniform. One characteristic of an ideal gas is that the internal energy depends only on temperature. When the two gases mix at constant temperature, the change in internal energy ($\Delta E$) is equal the change in enthalpy ($\Delta H$), which is equal to zero (i.e. $\Delta E = \Delta H = 0$). Thus, it can be concluded that enthalpy change is not the driving force for the spontaneous mixing of the gases.

Consider a similar experiment to the one above in which the gas is confined one chamber (A) separated from a chamber (B) that has been evacuated.

- **View animation!**

Upon opening the tap, gas molecules move from the left chamber (A) to the right chamber (B) resulting in an increase in disorder as each molecule has a larger volume to travel around

- no work is performed on the system or the surroundings
- heat is neither evolved nor absorbed in the process
- the process is spontaneous and irreversible.
There is evidently no change in energy. The process therefore is not spontaneous to minimize energy but is driven by the tendency to increase disorder. In both cases, the degree of randomness increases and the manner in which energy is distributed among the gas molecules changes. The driving force is the tendency of the molecules to achieve a maximum state of disorder.

The thermodynamic function that measures the degree of disorder of the system is called entropy, $S$. In mixing of the two gases in the example above, entropy of the system increases so that $\Delta S$ is greater than zero. The more disordered the state, the larger its entropy.

Entropy is a function that depends only on the initial and final state of the system. The change in entropy accompanying a processing can be written as

$$\Delta S = S_{final} - S_{initial}$$

The value of $S$ is positive if the degree of disorder increases, and is negative if disorder decreases. The reactions in the following example help illustrate the point.

**Example**

$$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$$

Entropy decreases since the liquid state is more ordered than the gaseous state.

$$2\text{NH}_4\text{NO}_3(\text{s}) \rightarrow 2\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$$

Entropy increases since the reaction yields a large amount of gas.

**Example 1**

Make qualitative predictions of entropy changes in the following processes.

(a) Reaction of sulphur dioxide with oxygen to form sulphur trioxide.

$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$$

(b) Vaporisation of one mole of water

$$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$$

**Solution**

(a) The number of moles of gaseous products is smaller than that of the reactants. Three moles of reactants giving 2 moles of products. Entropy decreases.

(b) Molecules in the vapour phase have greater freedom of movement. Entropy increases.
Practice problem 1

Suggest if there is an increase or decrease in entropy for the reaction shown below.

\[ \text{CuSO}_4(\text{s}) + \text{H}_2\text{O} \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \]

The change in entropy is directly proportional to the heat absorbed \((q)\) and inversely related to the temperature \((T)\). This can be expressed mathematically in the equation below.

\[ \Delta S = \frac{q_{\text{rev}}}{T} \]  

(2)

Since \(\Delta S\) is independent of the path taken, the route by which heat is absorbed or released must also be independent of the path. A way around this problem is to consider only one route by imposing deliberate restriction. We assume that the process proceeds via a reversible process so that the changes in heat are independent of the path taken, \(q = q_{\text{rev}}\).

The use of entropy as the sole criteria for predicting spontaneous processes is somewhat problematic. One classical example is the freezing of water spontaneously at -10 \(^\circ\)C. Ice is a more ordered state and yet the process occurs spontaneously. This apparent difficult is overcome by considering the change in entropy for both the system and the surroundings. The combined change of the system and surroundings entropy is called the entropy change of the universe expressed mathematically by

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

(3)

For a spontaneous (irreversible process), that produces an increase in entropy, in both the system and surroundings, the universe gains in entropy. We can therefore write that

\[ \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \]  

(4)

This is the mathematical representation of the second law of thermodynamics, which states that all spontaneous processes produce an increase in entropy of the universe.
This helps us explain the spontaneous freezing of water despite a having a negative entropy. In freezing heat is absorbed from the surroundings, the entropy change in the surroundings is therefore positive. In this case, the entropy increase in the surroundings is higher than the decrease in entropy of the system. Thus, the total entropy of the universe is positive when water freezes.

**Entropy and reversible processes**

In chemistry you have met a number of reactions that are reversible reactions. A common example is the reaction of hydrogen and nitrogen to give ammonia.

\[
H_2 (g) + N_2 (g) \rightleftharpoons NH_3 (g)
\]

The reaction can go in both directions to give either ammonia (forward) or hydrogen and nitrogen in the reverse direction. Another example of a reversible process is the phase transition of ice to liquid water. However, for ice to melt in a thermodynamic sense we would need to apply a minute amount of heat so that only a small amount of ice melts. If a small amount of heat was then withdrawn, the water would change back into ice. In a perfect reversible phase change of ice to water, the surroundings return to their initial state without affecting the rest of the universe. The entropy change in the system is given by

\[
\Delta S = \frac{\Delta H_{rev}}{T}
\]

where \(\Delta H_{rev} = q_{rev}\)

- **View animation!** Dissolution of a salt

**Example 2**

Calculate the entropy change when one mole of water is converted into water vapour at 100 °C. The heat of vaporisation is 40.6 kJ mol\(^{-1}\).

**Solution**

For a process occurring at constant temperature, the change in entropy, \(\Delta S\), is equal to the heat absorbed divided by temperature. At constant pressure \(q = \Delta H\). Thus

\[
\Delta S = \frac{\Delta H_{vap}}{T} = \frac{40.6 \times 10^3 \text{ J}}{373 \text{ K}}
\]

\[= 108.8 \text{ J K}^{-1}\]
Practice problem 2

The entropy change for the vaporisation of mercury is 86.5 J K\(^{-1}\)mol\(^{-1}\) at standard pressure. Calculate the boiling point if the enthalpy of vaporisation is 54.5 kJ mol\(^{-1}\).

(a) 6250 K
(b) 650 K
(c) 0.630 K
(d) 630 K

Effect of temperature and volume

The entropy of a system increases with increasing temperature. The number of ways in which energy is able to distribute also increases as temperature increases. When the temperature is low, approaching absolute zero, the kinetic energy of the random motion of the molecules is small. The number of ways to distribute energy are fewer and hence low entropy. Consider for example molecules in a solid. Molecules are at fixed locations within the lattice structure. These molecules have vibrational motion about their location. When the solid absorbs energy in form of heat, the vibrations of the molecules increases and the molecules are no longer found at a fixed point. The number of ways to spreading energy has increased.

Variation of entropy with temperature

The fact that entropy is influenced by temperature was highlighted qualitatively in the sections above. A quantitative analysis can be done by evaluating equation (2). For a system changing form an initial state with temperature \(T\) to a final temperature \(T_f\), the total entropy change for the process is found by integrating equation (2).

![View animation](Vibrational motion of molecules in a crystal structure.)
For a constant pressure process, the heat change $dq$ can be related to the heat capacity $C_p$, $dq = C_p dT$

So that

\[ S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p}{T} dT \]  

Similarly, for a process taking place at constant volume the heat capacity $(C_v)$ can be used in the expression

\[ S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_v}{T} dT \]  

The overall entropy change between a temperature $T_1$ and $T_2$ is found by integrating and finding the solutions for the constant pressure and volume processes as shown below.

Expression for constant pressure process

\[ S(T_2) = S(T_1) + C_p \ln \frac{T_2}{T_1} \]  

Expression for constant volume process

\[ S(T_2) = S(T_1) + C_v \ln \frac{T_2}{T_1} \]

These equations enable us to calculate the entropy change by measuring the heat capacity at different temperatures and evaluating the integrals. The change
in entropy is calculated as a difference in entropy between the temperatures of interest and absolute zero temperature, \( T = 0 \).

In moving from an initial temperature \( T_1 \) to a final temperature \( T_2 \), the process may pass through a number of phase transitions. The entropy associated with such transitions need to be taken into account in the calculation of the entropy change. For example, melting and boiling involve absorption of thermal energy (heat) with associated entropies of \( \frac{\Delta H_{\text{fusion}}}{T} \) and \( \frac{\Delta H_{\text{vaporization}}}{T} \) respectively. (11)

The overall entropy change for a constant pressure process from absolute zero \((T = 0)\) and entropy \( S(0) \) is given by

\[
\int S(T) - S(0) = \int_{T_{\text{initial}}}^{T_{\text{final}}} \frac{C_p(s)}{T} \,dT + \int_{T_{\text{fusion}}}^{T_{\text{vaporization}}} \frac{\Delta H_{\text{fusion}}}{T} + \int_{T_{\text{vaporization}}}^{T_{\text{final}}} \frac{\Delta H_{\text{vaporization}}}{T} + \int_{T_{\text{initial}}}^{T_{\text{final}}} \frac{C_p(g)}{T} \,dT
\]

This is shown graphically below.

**FIGURE 4**
Illustration of the mixing of two gases. Gases spontaneously migrate to opposite chambers once the valve is opened.

For rough estimations the area under the curve can be evaluated from a plot of \( C_p \,dT \) versus temperature.

**Example 3**

What is the change in entropy if a sample of solid magnesium is heated from 27 °C to 227 °C at 1 atm pressure. The specific heat capacity in region 0 – 600 °C varies according to the expression

\[ C_p = 26.0 + 5.46 \times 10^{-2} T - 28.6 \times 10^4 T^{-2} \]
Solution

The change in entropy in the temperature range 300 - 500 K can be calculated by applying equation (6).

\[ S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p}{T} dT \]

Making necessary substitutions,

\[ \Delta S = \int_{300}^{500} \frac{26.0}{T} dT + \int_{380}^{500} 5.46 \times 10^{-3} dT - \int_{300}^{500} 28.6 \times 10^4 \frac{dT}{T^3} \text{ J K}^{-1} \]

\[ = 26.0 \ln \left[ \frac{T}{300} \right]^{500} - 5.46 \times 10^{-3} \times \left[ \frac{T}{300} \right]^{500} + \frac{28.6 \times 10^4}{2} \left[ \frac{1}{T^2} \right]^{500}_{300} \text{ J K}^{-1} \]

\[ = 26.0 \ln \frac{500}{300} + 5.46 \times 10^{-3} \times 200 + 14.3 \times 10^4 \left[ \frac{1}{500^2} - \frac{1}{300^2} \right] \text{ J K}^{-1} \]

Practice problem 3

What is the change in entropy when 1 mole of water at 0 °C is heated to form steam at 110 °C at atmospheric pressure. The specific heat capacity is 4.18 J K^{-1} g^{-1} and the enthalpy of vaporisation is 2257 J g^{-1}.

(a) 5.8
(b) 140
(c) 132.1
(d) 8.3

Standard Entropies

Standard entropies are measured at 298 K and 1 atm with units of J K^{-1}. Using tabulated standard enthalpy values entropy changes for chemical reaction may be calculated as the difference between the sum of entropies of the products and the reactants.

\[ \Delta S^o = \sum S^o (\text{products}) - \sum S^o (\text{reactants}) \]
Effect of volume

An increase in the volume of a gas results in increased entropy. There are a greater number of possible states to gas molecules due to the larger space. Let us examine the expansion of an ideal gas confined in a piston.

For an ideal gas that expands at constant temperature the expression for the change in entropy is

$$\Delta S = \frac{1}{T} \int dq$$

We know from Unit II that for an isothermal reversible process

$$q_{rev} = -w = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln \frac{V_f}{V_i}$$

therefore the change in entropy can be expressed as

$$\Delta S = nRT \ln \frac{V_f}{V_i} \quad (15)$$

The equation can be transformed to relate to pressure using the volume-pressure inverse relationship.

$$\Delta S = nR \ln \frac{P_f}{P_i} \quad (16)$$

Absolute entropies

In the preceding sections, we have noted that as temperature is reduced, entropy is also reduced and reaches a minimum at absolute zero. This leads us to the statement of the third law of thermodynamics, which states that

at absolute zero the entropy of a perfect crystalline substance is zero.
**Gibbs free energy**

What factors ultimately determine that a reaction proceeds spontaneously? Spontaneous reactions are often exothermic (negative enthalpy, ΔH < 0) and are accompanied by an increase in entropy (increase in disorder, ΔS > 0). Both enthalpy and entropy appear to influence whether a reaction occurs spontaneously or not. Furthermore, spontaneous reactions are those where the final state (products) tend to be of lower energy than the initial state (reactants). Another factor for consideration in predicting if a chemical reaction or process is spontaneous is temperature. Some reactions are spontaneous only at high temperature and not at low temperature. Why?

We define a new function that reflects the balance between enthalpy, entropy and temperature, known as Gibbs free energy (G or simply Gibbs function).

\[
G = H - TS
\]

(17)

The expression reflects the stored energy (H), inherent disorder (S) at a given temperature (T in Kelvin). Since all the parameters in the equation are state functions so is \( G \). The change in Gibbs energy is

\[
\Delta G = \Delta H - T\Delta S
\]

(18)

at constant temperature. The change of free energy (energy available to do work) depends primarily on the magnitudes of \( \Delta H \) and \( T\Delta S \) (enthalpy and entropy terms).

Consider the reaction below.

\[
A + B \rightarrow C + D
\]

The reaction will behave in three ways depending on the value of \( \Delta G \).

\[
\begin{align*}
\Delta G < 0 & \quad \text{Reaction proceeds to give products } C, \ D \\
\Delta G = 0 & \quad \text{This represents an equilibrium condition in which the rates for the forward reactions is equal to that of the reverse reaction} \\
\Delta G > 0 & \quad \text{The reverse process is favoured to produce } A, \ B
\end{align*}
\]

In general we can conclude that the direction of spontaneous change in either the forward or reverse is that which leads to a decrease in free energy. In summary if:
ΔG < 0  Reaction is spontaneous in the forward direction.
ΔG = 0  Reaction is at equilibrium.
ΔG > 0  Reaction is spontaneous in reverse direction.

**Example 4**
In the sublimation of iodine crystals at 25 °C and atmospheric pressure, the process is accompanied by an enthalpy change of 39.3 kJ mol⁻¹ and an entropy change of 86.1 J K⁻¹. At what temperature will iodine crystals (solid) be in equilibrium with its vapour (gaseous iodine)?

The change in Gibb’s free energy (ΔG) is related to the change in enthalpy (ΔH) and entropy (ΔS) by

\[ ΔG = ΔH - TΔS \]

At equilibrium ΔG = 0 and T in the equation therefore the equilibrium temperature \( T_{eq} \). Thus,

\[ 0 = ΔH - T_{eq} ΔS \]

Solving for \( T_{eq} \)

\[
T_{eq} = \frac{ΔH}{ΔS} = \frac{39.3 \times 10^3}{86.1} = 454 \text{ K}
\]

**Practice problem 4**
Determine the melting point of sodium chloride (table salt) if 30.3 kJ is required to melt the crystals and that the process involves an increase in entropy of 28.2 J K⁻¹ mol⁻¹.

(a) 1.071
(b) 1070
(c) 1000
(d) 1075
Standard free energy, $\Delta G^\circ$

Gibbs function consists of two thermodynamic state functions, which can be used to calculate standard free energies. For a chemical reaction, the standard free energy of change ($\Delta G^\circ$) is related to the formation of the products from the reactants. The standard being defined as before for $\Delta H^\circ$ and $\Delta S^\circ$.

Properties of Gibbs function are very much similar to those of $\Delta H^\circ$ that is

- $\Delta G^\circ$ is zero for free energies of formation of elements in their standard state
- $\Delta G^\circ$ changes sign when the process is reversed but with the same magnitude
- For a process comprising several steps, the total free energy change is the sum of the $\Delta G^\circ$s associated with each individual steps

The free energy change for a chemical reaction can be calculated if the standard free energies of formation of the reactants and products are known.

$$
\Delta G^\circ = \sum a \Delta G_f^\circ (\text{products}) - \sum b \Delta G_f^\circ (\text{reactants})
$$

Free energy and equilibrium constant

The free energy of the reaction is zero at equilibrium, $\Delta G = 0$ and $\Delta G^\circ = 0$ for the standard state. The condition of equilibrium is attained when two opposing processes are occurring at equal rates. It is often desirable to describe equilibrium under non-standard conditions. The change in free energy under a variety of conditions is calculated in relation to its standard value.

$$
\Delta G = \Delta G^\circ + RT \ln Q
$$

For a reaction of the general type

$$aA + bB + \ldots \rightleftharpoons cC + dD + \ldots$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$
Where $Q$ is the reactions quotient calculated for a reaction under non-standard conditions. At equilibrium $Q_C = K_C$, $Q_P = K_P$, and $Q = K_{eq}$. For the condition where $\Delta G = 0$, equation (20) becomes

$$0 = \Delta G^\circ + RT\ln Q$$

so that

$$\Delta G^\circ = - RT\ln K_{eq}$$

Equation (23) relates the standard free energies and to measurable quantities $T$ and the equilibrium composition.

All chemical reactions comprise a forward and a reverse reaction to varying extents. The system is always seeking a minimum in energy. Therefore, the direction of spontaneous change is one that decreases Gibbs function from either direction as shown in Figure 7. The graph depicts the change in free energy for a hypothetical reaction. The free energy is observed to be decreasing both from the left and right. A minimum is reached at some point which corresponds to the equilibrium point. The plot shows that the standard free energy is the difference between the standard molar free energies of formation of the reactants and products.

The equilibrium constant for a reaction can be calculated by solving equation (23).

$$K = e^{-\frac{\Delta G^\circ}{RT}}$$

Example 5

The reaction of hydrogen and iodine to form hydrogen iodide at 763 K has a standard free energy of formation $-12.1\text{kJ mol}^{-1}$.

$$\text{H}_2 (\text{g}) + I_2 (\text{g}) \rightarrow 2 \text{HI (g)}$$
What is the equilibrium constant for the reaction?

**Solution**

At equilibrium the standard free energy of formation is given by

\[ \Delta G^\circ = -RT \ln K_{eq} \]  

equation

In this example \( \Delta G^\circ = -12.1 \text{ kJ mol}^{-1} \), \( T = 763 \text{ K} \) and \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \). Hence

\[
\ln K = -\frac{2 \times (-12.1 \times 10^3 \text{ J mol}^{-1})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 763 \text{ K}}
\]

\[ \ln K = 3.81 \]

Taking the antilog \( K = 45 \)

**Practice problem 5**

Dinitrogen tetroxide is a common rocket fuel, which at 25 °C dissociates into nitrogen dioxide forming an equilibrium between the two gases. The equilibrium mixture depends on the temperature of the mixture. What is the change in Gibbs free energy if the quantities of the two gases present in a 1 L container are 11.5 g N\(_2\)O\(_4\) and 2.54 g NO\(_2\). The standard Gibbs free energy for the reaction is +4853 J.
Learning activity # 5

Title of Learning Activity: Chemical kinetics

Specific Teaching and Learning Objectives

When you have completed this activity you should be able to

- Explain and use the terms: rate of reaction, order of reaction, rate constant, half-life of a reaction, rate determining step and activation energy
- Explain the effects of temperature, pressure and concentration on the rates of reaction
- Determine the order of reaction from experimental data

Summary of the learning activity

The subject of this unit, chemical kinetics, is concerned with how fast chemical reactions take place. What factors affect the rate at which a reaction proceeds? An understanding of the rates of change is essential in industry where control of reaction speeds is important. In manufacturing for example, a reaction needs to proceed at a pace fast enough to be economically feasible but at the same time safe. Knowledge of chemical kinetics can also enable optimisation of a reaction to obtain higher yields. The rates of reaction can give us an insight of how the reaction proceeds stepwise at a microscopic scale.

Key concepts and terms

- Activation energy
- Catalyst
- Collision theory
- Elementary process
- Half-life
- Heterogeneous catalyst
- Homogenous catalyst
- Integrated rate laws
- Order of reaction
- Rate determining step
- Rate law
- Rate of reaction
- Transition state
- Transition state theory
List of relevant readings

- Chemical Kinetics

List of relevant resources

- Chem1 Virtual Textbook
  [http://www.chem1.com/acad/webtext/virtualtextbook.htm](http://www.chem1.com/acad/webtext/virtualtextbook.htm)
- Chemistry Experiment Simulations and Conceptual Computer Animations

Multimedia Resources

- Computer with internet access to enable access to open source learning material and interactive learning through email, video conferencing and use of CD-ROMs
- QuickTime Movie Player Software
- Shockwave Player Software
- Macromedia Flash Player Software

List of relevant useful links

- The Catalyst: Chemistry Resources For Teachers
  [http://www.thecatalyst.org](http://www.thecatalyst.org)
- Science Resource Centre
  [http://chem.lapeer.org](http://chem.lapeer.org)
- Chemistry Teaching Web Sites
  [http://people.moreheadstate.edu/fs/h.hedgec/sciteach.html](http://people.moreheadstate.edu/fs/h.hedgec/sciteach.html)
- Mitopencourseware
  [http://ocw.mit.edu](http://ocw.mit.edu)
- Chemical Kinetics
  Wikipedia, the free encyclopedia.htm
Detailed description of the activity

This activity looks at speeds of reactions and what factors influences them. What laws are at play to enable one control the reaction rate? In this Unit, you will study how to measure the rate of reaction and establish what rate law (expression) governs a particular reaction. Integrated rate laws are introduced and will be used to establish the status of the reaction at certain times as the reaction proceeds. Such information is important in many areas, for example in establishing expiry dates for various perishable products, rates of environmental degradation and rate of absorption of drugs in the body.

Formative evaluation

• As you go through this learning activity you will come across chemical tasks to test your conceptual understanding of the subject matter.
• Rapid quizzes are provided to check your understanding.
• Practical experiments will be given to evaluate your understanding of theory-practise relations
• Simulated reaction kinetics experiments accompanied with exercise.

Learning activities

How fast?

Many of the chemical processes that we come across everyday, natural and synthetic, progress at different speeds. For example, souring of milk, fermentation, and environmental degradation of waste plastics takes place at relatively slow pace. On the other hand, some reactions are quite fast. Reactions taking place in pyrotechnics (fireworks) are rapid and spectacular unlike the spoiling of milk. A number of factors affect the speeds of chemical change, which are easily deduced from our daily experiences. Milk and many dairy products spoil very quickly when left at room temperature but keep quite well in a refrigerator. Some drugs need to be kept in a “cool place” to avoid rapid degradation. The greenhouse gas, nitrogen dioxide, is not produced in significant amounts at room temperature. However, the reaction becomes highly favourable in an internal combustion engine due to high temperature and pressure. Pressure, temperature and concentration influence the rates of reactions as seen from the preceding examples.
Why study reaction kinetics?

In chemical kinetics we study factors that control rates of chemical change. Understanding these factors has significance in the manufacturing industry where feasibility of process and rates of production are important. Knowledge of reaction kinetics in drugs is important not only from a therapeutic viewpoint but also in issues of drug stability and mode of degradation.

Measuring rates of reaction

Reaction rates measure how fast a reaction is progressing through monitoring of a suitable parameter that changes with evolution of time. Such parameters may be the volume, pressure or concentration of the reaction system. Consider a hypothetical reaction involving reactants ‘A’ giving products ‘B’.

\[ A \rightarrow B \]

The rate can be measured by monitoring how fast ‘A’ molecules are consumed and ‘B’ produced. The rate at which reactants appear and disappear in the reaction system is a measure of the rate of reaction. In the hypothetical example, we can measure the rate of change in number of moles with time.

\[
\text{Average rate} = \frac{\text{change in number of moles (} n_A \text{)}}{\text{change in time}} = \frac{n_B}{\Delta t} = -\frac{n_A}{\Delta t}
\]

where \( n_A \) and \( n_B \) are the numbers of species ‘A’ and ‘B’ respectively. The rate may also be reflected in terms of concentrations of the reactants and products.

**FIGURE 1**

Plot (a) and (b) show the variation of concentration with time. Plot (a) shows the calculation of average rate while plot (b) indicates the instantaneous rate.
Reactions in general initially start-off rapidly but slow down with time since the rate depends on the concentration of reactants. As the concentration of reactants decreases so does the rate of reaction.

**Example 1**

The decomposition of $\text{N}_2\text{O}_5$ at 45 °C was followed and the following data obtained.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>0</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. $\text{N}_2\text{O}_5$ (mol dm$^{-3}$)</td>
<td>0.250</td>
<td>0.222</td>
<td>0.196</td>
<td>0.173</td>
<td>0.153</td>
<td>0.136</td>
<td>0.120</td>
</tr>
</tbody>
</table>

(a) Calculate the average rate of reaction between the 400 and 800 seconds.

(b) What is the rate of reaction at 600 seconds?

**Solution**

(a) Prepare a graph of concentration of $\text{N}_2\text{O}_5$ against time. The plot obtained is shown below.

The average rate between 400 and 600 second is $\Delta$concentration/$\Delta$Time

$= (0.196-0.153)/800-400) = 2.14 \times 10^{-4}$ mol dm$^{-3}$ s$^{-1}$

(b) The rate at 600 s is determined by drawing a tangent to the curve at that point and calculating the slope.
Rates and orders of reaction: relationship between reactant concentrations and time

Consider the reaction involving the dissociation of HI into H₂ and I₂ as shown below.

\[ 2\text{HI} (g) \rightarrow \text{H}_2 (g) + \text{I}_2 (g) \]

The rate of reaction may be expressed as

\[ \text{Rate} = \frac{-1}{2} \frac{\Delta \text{[HI]}}{\Delta t} = \frac{\Delta \text{[H}_2\text{]}}{\Delta t} = \frac{\Delta \text{[I}_2\text{]}}{\Delta t} \]  \hspace{1cm} (2)

For the general reaction

\[ a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D} \]

The rate can be variously represented as shown below.

\[ \text{Rate} = \frac{1}{a} \frac{\Delta \text{[A]}}{\Delta t} = \frac{1}{b} \frac{\Delta \text{[B]}}{\Delta t} = \frac{1}{c} \frac{\Delta \text{[C]}}{\Delta t} = \frac{1}{d} \frac{\Delta \text{[D]}}{\Delta t} \]  \hspace{1cm} (3)

Where \([A], [B], [C]\) and \([D]\) are concentrations of the reactants and products with \(a, b, c\) and \(d\) as reaction coefficients.

For a small (infinitesimal) change in concentration and time, the rate is expressed as

\[ \text{Rate} = -\frac{1}{a} \frac{d\text{[A]}}{dt} \]  \hspace{1cm} (4)

A purpose in the study of chemical kinetics is to be able to predict how the speed of the reaction behaves with changes in the concentration of the reactants. For many reactions, the rate is found to be proportional to the product of the molar concentrations of the reactants, each raised to an exponent or power as shown in equation (5). The expression that gives this relationship is known as the rate law expression and is determined experimentally. It is usually of the general form
Rate = \( k[A]^n[B]^m \) \hspace{1cm} (5)

where \( n \) and \( m \) are called orders of reaction with respect to \( A \) and \( B \) correspondingly. The overall order of reaction is \( n + m \). The proportionality constant \( k \) is the rate constant for the reaction. It should be noted that orders of reaction are determined experimentally and are not coefficients of the reaction.

**Zero order**

The zero order reaction rate has a rate equation in which the sum of the exponents in the expression is equal to zero i.e. \( n + m = 0 \). For example, for a reaction of the type

\[ A \rightarrow \text{products} \]

the rate equation can be expressed as

\[
\text{Rate} = -\frac{d[A]}{dt} = k[A]^0
\]

or

\[
-\frac{d[A]}{dt} = k
\]

(6) \hspace{1cm} (7)

Equation (7) can be integrated to obtain an expression that allows the prediction of the concentration at a given time, \( t \).

\[
\int_{[A]_0}^{[A]} d[A] = k \int_0^t dt
\]

\[
[A]_t + [A]_0 = -kt
\]

(8) \hspace{1cm} (9)

\[
[A] = -kt + [A]_0
\]

(10)
The equation is similar to the equation of a straight line: \( y = mx + c \).

The rate constant \( k \) is derived to be:

\[
k = \frac{[A]_0 - [A]_t}{t}
\]  

(11)

For a zero order reaction, \( k \) has units \( \text{mol L}^{-1} \text{s}^{-1} \).

An important characteristic of rates of reaction is the half-life. The half life is defined as the time that is required for one-half of the reactant to be consumed or disappear and is designated \( t_{\frac{1}{2}} \). For zero order of reaction the half-life of the equation (10) takes the form:

\[
[A]_{\frac{1}{2}} = [A]_0 - k t_{\frac{1}{2}} + [A]_0
\]

(12)

Solving for \( t_{\frac{1}{2}} \):

\[
t_{\frac{1}{2}} = \frac{1}{k}[A]_0
\]

(13)

**First order reaction**

The reaction is first order when the sum of the exponents are equal to 1 i.e. \( n + m = 1 \).

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

\( A \rightarrow \) products

For the hypothetical reaction above the rate is:

\[
\text{Rate} = -\frac{d[A]}{dt} = k[A]
\]

(14)

Integration gives us
whose solution is a straight line graph of the type $y = mx + b$.

\[ \ln [A]_t - \ln [A]_0 = -k(t - 0) \quad (16) \]

\[ \ln [A]_t = \ln [A]_0 - kt \quad (17) \]

\[ \ln [A]_t = (-k)(t) + \ln [A]_0 \]

or

\[ \log [A]_t = \log [A]_0 - \frac{kt}{2.303} \quad (18) \]

Solving for $k$ gives us

\[ k = \frac{2.303 \log [A]_0}{t} \quad (19) \]

Units of $k$ for a first order reaction are s$^{-1}$.

At half-life, $t_{\frac{1}{2}}$, $[A]_{t_{\frac{1}{2}}} = \frac{1}{2} [A]_0$ and substituting in equation (16) we obtain

\[ \ln \frac{1}{2} [A]_0 = \ln [A]_0 - kt_{\frac{1}{2}} \quad (20) \]

\[ \ln \frac{1}{2} [A]_0 = -kt_{\frac{1}{2}} \quad (21) \]

and solving for $t_{\frac{1}{2}}$. 
The above equation shows that the half-life for a first order reaction is constant.

**Second order reactions**

Bimolecular reactions, which occur when two molecules come together, are frequently described as second order. The sum of exponents are equal to two i.e. \( n + m = 2 \).

\[ A + B \rightarrow \text{products} \]

In the above hypothetical reaction, the rate depends on the product of concentrations of \([A]\) and \([B]\) each raised to the power of one.

\[
-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]
\]  

(23)

Let \( a \) and \( b \) be the initial concentration of \( A \) and \( B \) respectively, \( x \) is the concentration of species reacting in time \( t \). We can write that \([A]_t = (a - x)\) and \([B]_t = (b - x)\). The rate equation maybe expressed as

\[
\frac{dx}{dt} = k(a - x)(b - x)
\]  

(24)

If \( a = b \) then

\[
\frac{dx}{dt} = k(a - x)^2
\]  

(25)

Integrating the above equation

\[
\int_0^x (a - x)^2 \, dx = k \int_0^t dt
\]  

(26)

giving the solution
\[
\frac{1}{a - x} - \frac{1}{a - 0} = kt \tag{27}
\]
Solving for \( k \)

\[
k = \frac{1}{at} \left( \frac{x}{a - x} \right) \tag{28}
\]

\[
k t = \frac{x}{a(a - x)} \tag{29}
\]
Equation (28) maybe re-written as

\[
k t = \left[ A \right]_0 - \frac{1}{2} \left[ A \right]_0 \tag{30}
\]
Units of \( k \) are \( L \text{ mol}^{-1} \text{s}^{-1} \).

The half-life for the second order reaction is given by

\[
t_\frac{1}{2} = \frac{1}{k} \left[ A \right]_0 - \frac{1}{2} \left[ A \right]_0 \tag{31}
\]

\[
t_\frac{1}{2} = \frac{1}{k} \left[ A \right]_0 \tag{32}
\]
The half-life for a second order reaction is not a constant but depends on the initial concentration and on the rate constant.

**Determination of order of reaction**

The order of reaction can be determined using a variety of techniques that are outlined in brief in the section that follows.

- **Substitution method**

In the substitution method experimental data is substituted into the integrated rate equation that describes different orders of reaction. The equation in which the calculated values of \( k \) is constant is considered as the appropriate order.
The following example illustrates the method. Harned (1918) examined the decomposition of KI catalysed decomposition of hydrogen peroxide and obtained data shown in the Table below. The calculated values of $k$ using the integrated equation for the first order reaction gave values of $k$ which are constant. It can therefore be concluded that the reaction follows first order reaction kinetics.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$a - x$</th>
<th>$k$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>57.90</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>50.40</td>
<td>0.0278</td>
</tr>
<tr>
<td>10</td>
<td>43.90</td>
<td>0.0277</td>
</tr>
<tr>
<td>25</td>
<td>29.10</td>
<td>0.0275</td>
</tr>
<tr>
<td>45</td>
<td>16.70</td>
<td>0.0276</td>
</tr>
<tr>
<td>65</td>
<td>9.60</td>
<td>0.0276</td>
</tr>
</tbody>
</table>

• Graphical method

Experimental data is tested in the various integrated rate equations. All integrated rate equations resemble the equation of a straight line. Data for which concentration is plotted against $t$ for a particular integrated rate law gives a straight line, is then the order of reaction.

<table>
<thead>
<tr>
<th>Graph giving straight line</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration versus time</td>
<td>Zero order</td>
</tr>
<tr>
<td>Log [A], versus time</td>
<td>First order</td>
</tr>
<tr>
<td>$1/(a - x)$ versus time</td>
<td>Second order</td>
</tr>
</tbody>
</table>

**Example 2**

The decomposition of a sample of glucose of 0.056 M at 140 °C in aqueous solution containing 0.35 HCl was followed and gave data as shown below.
<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Conc. glucose remaining (mol dm$^{-3} \times 10^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>5.52</td>
</tr>
<tr>
<td>2</td>
<td>5.31</td>
</tr>
<tr>
<td>3</td>
<td>5.18</td>
</tr>
<tr>
<td>4</td>
<td>5.02</td>
</tr>
<tr>
<td>6</td>
<td>4.78</td>
</tr>
<tr>
<td>8</td>
<td>4.52</td>
</tr>
<tr>
<td>10</td>
<td>4.31</td>
</tr>
<tr>
<td>12</td>
<td>4.11</td>
</tr>
</tbody>
</table>

(a) Determine the order of reaction and the rate constant for the reaction.
(b) What is the half-life for the reaction?

**Solution**

(a) The graphical method can be used to test the data in the various integrated rate equations. Data for which concentration against time plot best fits to a straight line gives the correct order of reaction. In this case, the reaction is first order. The rate constant is determined from the slope of the graph as $k = 0.026 \text{ hrs}^{-1}$.

(b) For the first order reaction the half-life is given by

\[
\frac{t}{2} = \frac{0.693}{k}.
\]

\[
= \frac{0.693}{0.026} \text{ hrs}^{-1}.
\]

\[
= 26.6 \text{ hrs}
\]
Theories of reaction rates

For a chemical reaction to occur the reacting molecules must meet each other by colliding. However, not all collisions will result in a chemical change. Two factors are of prime importance for a reaction to take place.

- The colliding molecules must have sufficient kinetic energy to effect disruption of bonds and the formation of new ones. In order to react they must have a total kinetic energy equal to or greater than the activation energy \((E_a)\). Activation energy is the minimum amount of energy required to initiate a chemical reaction.
- The molecules must have the correct orientation on collision for a reaction to occur.

It follows that not all collisions will result in a chemical reaction. Only a certain fraction of molecules with sufficient kinetic energy, called the activation energy \((E_a)\) and the right orientation produce a chemical reaction. This theory, which postulates how reactions occur in terms of molecular collisions, is known as the collision theory.

Orientation of collision

Only molecules with the appropriate orientation lead to formation of a new product. Other molecules may collide but will simply bounce off. Consider for example the reaction involving an addition reaction of an alkene (propene) and hydrogen bromide.

![View animation! Colliding molecules](image)

Only the collision indicated above could possibly result in a chemical reaction.
Activation energy

Despite being correctly oriented, a collision may not result into a successful reaction if the combined kinetic molecular energy ($E_a$) is not above a certain minimum. During a collision, molecules come together and chemical bonds are stretched, broken and reorganised. The molecular kinetic energy possessed by the colliding molecules changes into potential energy in the products as new bonds are formed. As molecules come together in a collision, the overall kinetic molecular energy must be sufficient to overcome the repulsion due to the electron clouds around the molecules. The molecules must be moving fast enough with sufficient energy for their nuclei and electrons to overcome the repulsions to break bonds and make new ones.

Effect of temperature on rates of reaction

Any factor that increases the rate of collisions will result in an increase in the rate of reaction. It is commonly known that increasing temperature results in an increase in the rate of reaction. Indeed the rule of thumb is that the rate doubles for every ten (10) degree increase in temperature.

Boltzmann distributions showed us that molecules of a gas would have a distribution of molecular kinetic energies.

**FIGURE 3**
Diagram show distribution of molecular kinetic energies at two temperature $T_1$ and $T_2$, $T_2 > T_1$.

**FIGURE 4**
Illustration of the transition state theory. An activated complex forms prior to rearrangement of bonds and redistribution of energy in the products.

Transition state theory

This theory proposes that intermediate species form between reactants and products in a chemical reaction. The intermediate species in the transition state is known as the activated complex. The activated complex can either dissociate back into reactants or into products as shown below.

Two species reacting  Activated complex  Products
A potential energy diagram maybe used to illustrate the reaction profile indicating the variation of potential energy as the reaction progresses.

Since temperature increases the rate of reaction and so it should also have an effect on the rate constant and the activation energy. The relation for the three parameters is according to the expression

\[ k = A e^{\frac{-E_a}{RT}} \]  

(33)

The parameter \( A \) is called the frequency factor or pre-exponential factor and \( E_a \) is the activation energy, collectively known as Arrhenius parameters.

The equation is usually used in logarithmic form as

\[ \ln k = \frac{-E_a}{RT} + \ln A \]  

(34)

\[ \ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A \]  

(35)

Here it is written as a linear equation. A plot of \( \ln k \) versus \( 1/T \) yields a straight. Activation energy can therefore be determined graphically using this method.

The activation energy can also be calculated by measuring rate constants at two different temperatures through the expression

\[ \ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]  

(36)
Example 3

The data below shows the variation of the rate constant at different temperatures for the alkaline hydrolysis of ethyl benzoate.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>k x 10^4 (mol dm^-3 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.02</td>
</tr>
<tr>
<td>15.0</td>
<td>12.74</td>
</tr>
<tr>
<td>24.9</td>
<td>28.68</td>
</tr>
<tr>
<td>40.13</td>
<td>95.6</td>
</tr>
</tbody>
</table>

Determine the activation energy for reaction.

Solution

Since a series of data is given, a graphical determination is ideal. (Use excel spreadsheet or any other suitable tool for graphing)

From equation (35), a plot of $\ln k$ versus $1/T$ should yield straight from which $E_a$ and $k$ can be determined.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>T (K)</th>
<th>1/T (K^-1)</th>
<th>K (mol dm^-3 s^-1) lnk</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>273.9</td>
<td>3.65 x 10^-3</td>
<td>3.03 x 10^-3</td>
</tr>
<tr>
<td>15.00</td>
<td>288.0</td>
<td>3.47 x 10^-3</td>
<td>1.27 x 10^-3</td>
</tr>
<tr>
<td>24.90</td>
<td>297.9</td>
<td>3.36 x 10^-3</td>
<td>2.87 x 10^-3</td>
</tr>
<tr>
<td>40.13</td>
<td>313.1</td>
<td>3.19 x 10^-3</td>
<td>9.56 x 10^-3</td>
</tr>
</tbody>
</table>

A plot of $\ln k$ versus $1/T$ will give a straight line.

The slope is $-Ea/R$ according to the Arrhenius equation. From the plot above

$Ea = - \text{slope} \times R = (-1.5/0.0002) \times 8.314$

$= 62.3 \text{ kJ mol}^{-1}$
Practice problem 3

The activation energy and enthalpy of reaction for the gas phase reaction

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

are 134 kJ and –241 kJ respectively. The frequency factor \( A \) is given as \( 1.3 \times 10^{10} \).

(a) What is the rate constant for the reaction at 700 K

(b) At what temperature would the rate of reaction be ten (10) times the rate at 700 K?

(c) Use an energy diagram to profile the reaction clearly indicating \( E_a \) and \( \Delta H \).

Interactive Exercises:

Rates of Reactions

Initial rates of reaction

Iodine clock
XV. Synthesis of the Module

Having gone through this module you should be better placed to explain the properties of gases based on the accepted explanation of why gases behave as they do. The laws that govern their behaviour, which is based on the behaviour of their individual molecules, have played a very important role in the development of the atomic theory of matter and the kinetic molecular theory of gases. The ideal gas law describes how to calculate the number of moles in a sample of gas from its temperature, volume and pressure.

The module introduces the concepts of work, heat and energy and describes briefly the relationships among them, within the context of open, closed and isolated systems. The various sections of the module examined more closely the relationships and laws that govern chemical reactions. Using the concepts of enthalpy, entropy and free energy in thermodynamics, you should be able predict whether a reaction will proceed spontaneously or not. Furthermore, you should be able to explain why chemical processes tend to favour one direction based on your knowledge of the second law of thermodynamics. Once started, how fast does the reaction proceed? What are the conditions that affect the speed of reaction? Chemical kinetics, also the subject of this module, provides answers to the question about the speed of a reaction.
XVI. Summative Evaluation

1. The ratio of the speed of helium atoms to oxygen molecules if both gases are at the same temperature is (a) 2.82 (b) 0.355 (c) 2 (d) 0.5

2. A 12 litre sample of hydrogen at a pressure of 760 mmHg is transferred to a new container. The pressure after the transfer is 700 mmHg. What is the volume of the new container if the temperature remains constant? (a) 10.74 L (b) 13.41L (c) 11.05 L (d) 13.03 L

3. A 12 litre sample of helium at a temperature of 25 °C is transferred to a 10 litre container. What is the resultant temperature after the transfer if the pressure remains constant? (a) -20 °C (b) 91 °C (c) - 25 °C (d) 80 °C

4. A 20 litre sample of the element which spells danger to Superman is at a temperature of 30 °C and under a pressure of 800 mmHg. It is transferred to a new container and the temperature rises to 60 °C while the pressure changes to 600 mmHg. What is the volume of the new container? (a) 29.3 L (b) 16.5 L (c) 36.6 L (d) 27.5 L

5. In a chemical reaction the difference between the potential energy of the products and the potential energy of the reactants is called (a) activation energy (b) kinetic energy (c) activated complex (d) heat of reaction.

6. The enthalpy of a reaction may also be called the (a) free energy (b) heat of Reaction (c) entropy (d) additivity.

7. Heat of reaction, ΔH, is equal to (a) H(products) + H(reactants) (b) H(products) - H(reactants) (c) H(products) X H(reactants) (d) H(products) / H(reactants).

8. Equilibrium is reached in all reversible chemical reactions when the (a) forward reaction stops (b) reverse reaction stops (c) concentrations of the reactants and the products become equal (d) rates of the opposing reactions become equal

9. When solid ammonium chloride is dissolved in a beaker of water the temperature decreases. The reaction occurring in the beaker is (a) exothermic and spontaneous (b) exothermic and not spontaneous (c) endothermic and spontaneous (d) endothermic and not spontaneous.

10. In order for reactions to occur (a) the reactants must be gases (b) chemical bonds must break (c) the temperature must be high (d) collisions must occur between molecules

11. If a reaction has a negative heat of reaction and a negative entropy the reaction will (a) occur at high temperatures (b) occur at low temperatures (c) occur at all temperatures (d) never occur
12. Which one of the following does not affect the rate of a reaction. Whether it will increase or decrease the reaction rate. (a) increase concentration (b) increase surface area - increase rate (c) polarity (d) increase temperature

13. Consider the elementary reaction: A + B \rightarrow C. Use the following data to determine the variables p, q, and k in the following rate equation:

\[ R = k[A]^p[B]^q \]

<table>
<thead>
<tr>
<th>[A]</th>
<th>[B]</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>17.6</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4.4</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>26.4</td>
</tr>
</tbody>
</table>

(i) Value of k is (a) 1.47 (b) 1.74 (c) 1.40 (d) 1.64
(ii) Values of p and q are (a) 1 and 2 (b) 1 and 3 (c) 1 and 2.58 (d) 2 and 1

14. A hypothetical decomposition reaction of substance A, A \rightarrow B + C, is known to be first order with respect to the reactant. The data below was collected on investigation of the reaction:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[A] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
</tr>
</tbody>
</table>

What is the half-life for the reaction? (a) 3.46 min (b) 0.29 min (c) 3.46 min −1 (d) 3.46 s

15. An experiment was carried out to determine the activation A + B \rightarrow C. The following data was collected:

<table>
<thead>
<tr>
<th>Trial</th>
<th>Rate constant (k)</th>
<th>Temp (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.001127</td>
<td>100.0</td>
</tr>
<tr>
<td>2</td>
<td>0.010830</td>
<td>150.0</td>
</tr>
<tr>
<td>3</td>
<td>0.033570</td>
<td>200.0</td>
</tr>
<tr>
<td>4</td>
<td>0.066180</td>
<td>250.0</td>
</tr>
</tbody>
</table>

The activation energy was determined to be (a) 5645 J/mol (b) 5600 J/mol (c) 5700 J/mol (d) 11 290 J/mol
16. Given the reaction: \( \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + 57.8 \text{ kcal} \). If the activation energy for the forward reaction is 40.0 kilocalories per mole, the activation energy for the reverse reaction, in kilocalories per mole, will be (a) 17.8 (b) 30.0 (c) 60.0 (d) 97.8

17. A reaction takes place inside a cylinder with a piston. The gas expands from an initial state 1 for which \( E_1 \) is 70 kJ to state 2 for which \( E_2 \) is 20 kJ. If during the expansion the gas does 60 kJ of work on the surroundings, determine the quantity of heat transferred during the process. (a) 130 kJ (b) 80 kJ (c) 20 kJ (d) 30 kJ

18. Given the following thermochemical data for the reaction

\[
\text{CO (g) + Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})
\]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta^\circ \text{J K}^{-1} \text{mol}^{-1} )</th>
<th>( n \Delta H_f \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>197.7</td>
<td>-110.4</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>222.8</td>
<td>0</td>
</tr>
<tr>
<td>COCl(_2)</td>
<td>288.8</td>
<td>-222.8</td>
</tr>
</tbody>
</table>

Calculate the standard free energy change associated with this reaction. (a) - 288.8 (b) - 73.15 (c) 36.3 (d) + 73.15

19. Determine the free energy when water is transformed from liquid to gaseous state at 100 °C and 1 atm according to the equation shown below?

\[
\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)} \quad \Delta H = 40.6 \text{ kJ mol}^{-1}
\]

(a) 3625 (b) 0 (c) 26.00 (d) 19440

20. The dimerization of NO\(_2\) to N\(_2\)O\(_4\)

\[
\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4
\]

has \( k = 8.85 \) at 298 K and \( k = 0.0792 \) at 373 K. Calculate the change in enthalpy, \( \Delta H^\circ \), for the reaction. (a) 58.2 (b) 60.0 (c) -58.2 x 10\(^1\) (d) 58.2 x 10\(^1\)
Answers Key

1. (a) 2.82
2. (d) 13.03l
3. (c) - 25 °C
4. (c) - 25 °C
5. (d) heat of reaction
6. (b) heat of Reaction
7. (b) H(products) - H(reactants)
8. (d) rates of the opposing reactions become equal
9. (c) endothermic and spontaneous
10. (d) collisions must occur between molecules
11. (b) occur at low temperatures
12. (c) polarity
13. (i) (a) 1.47 (ii) (c) 1 and 2.58
14. (a) 3.46 min
15. (a) 5645 J/mol
16. (a) 17.8
17. (c) - 20 kJ
18. (b) 0
19. (c) - 58.2
20. (c) - 58.2 x 10³
XVII. References


Animation and simulations Credits

Breenbowe, T. Chemistry Experiment Simulations and Conceptual Computer Animations, Chemical Education Research Group, Department of Chemistry, 3051 Gilman Hall, Iowa State University.
http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/simDownload/index4.html#kinetics
XVIII. Student Records

Name of the EXCEL file: *My Records*

Distribution of Marks

<table>
<thead>
<tr>
<th>Mode of Assessment</th>
<th>Marks</th>
</tr>
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<tr>
<td>Assignments/quizzes</td>
<td>5 %</td>
</tr>
<tr>
<td>Practicals/exercises</td>
<td>15 %</td>
</tr>
<tr>
<td>Tests</td>
<td>20 %</td>
</tr>
<tr>
<td>Final examination</td>
<td>60 %</td>
</tr>
</tbody>
</table>
XIX. Main Author of the Module

The author of this module, Chemistry 5, Physical Chemistry 1, is Dr Onesmus Munyati, a lecturer in the Department of Chemistry at the University of Zambia, Lusaka, Zambia. I hope you have enjoyed going through the sections in this module. Your comments and suggestions on how to improve the module are welcome. Contact at omunyati@natsci.unza.zm.
XX. File Structure

Chemistry 5, Physical chemistry (WORD)

F001Properties of Gases (PDF)
F002Chemical energetics (PDF)
F003Thermodynamic Equilibrium (PDF)
F004Gas Laws (PDF)
F005Boyle's law (Shockwave flash)
F006Charles law (Shockwave flash)
F007Effusion (Shockwave flash)
F008Reacting gases (Quicktime movie)
F009work heat 1stLaw (PDF)
F010Isothermal expansion (PDF)
F011Heat solution (Shockwave flash)
F012Thermochemistry (PDF)
F013Calorimetry (Shockwave flash)
F014Criteria spontaneous change (PDF)
F015Absolute entropy (PDF)
F016Expansion (Shockwave flash)
F017Increased entropy (PDF)
F018Increase vibrations (Shockwave flash)
F019NO+O3single rxn (HTML)
F020Rate chemical rxn (Shockwave flash)
F021kinetics_initial_rates (Shockwave flash)
F022Iodine clock (Shockwave flash)
QuickTimeInstaller (Movie player)
My Records (Excel student records)
SW Standalone Installer (Flash player)