CHEMISTRY

STUDENT TEXTBOOK

GRADE 11

Authors, Editors and Reviewers:

J.L. Sharma (Ph.D.)
Kefyalew Ketema (B.Sc.)
Yared Merdassa (M.Sc.)
Mesfin Redi (Ph.D.)

Evaluators:

Nega Gichile
Mahtot Abera
Solomon Haileyesus

FEDERAL DEMOCRATIC REPUBLIC OF ETHIOPIA
MINISTRY OF EDUCATION

Published E.C. 2002 by the Federal Democratic Republic of Ethiopia, Ministry of Education, under the General Education Quality Improvement Project (GEQIP) supported by IDA Credit No. 4535-ET, the Fast Track Initiative Catalytic Fund and the Governments of Finland, Italy, Netherlands and the United Kingdom.

The Ministry of Education wishes to thank the many individuals, groups and other bodies involved – directly and indirectly – in publishing this textbook and the accompanying teacher guide.

Copyrighted materials used by permission of their owners. If you are the owner of copyrighted material not cited or improperly cited, please contact with the Ministry of Education, Head Office, Arat Kilo, (PO Box 1367), Addis Ababa, Ethiopia.

PHOTO CREDIT: Encarta ® Encyclopedia, 2009 edition.
AAU (Addis Ababa University, Chemistry Department)

Developed and Printed by

STAR EDUCATIONAL BOOKS DISTRIBUTORS Pvt. Ltd.
24/4800, Bharat Ram Road, Daryaganj,
New Delhi – 110002, INDIA

and

ASTER NEGA PUBLISHING ENTERPRISE
P.O. Box 21073
ADDIS ABABA, ETHIOPIA

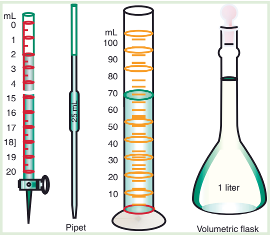
Second Edition 2007 (E.C.),
By Tan Prints India Pvt. Ltd.

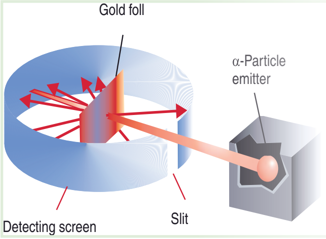
Under GEQIP Contract No. ET-MoE/GEQIP/IDA/ICB/G01/09.

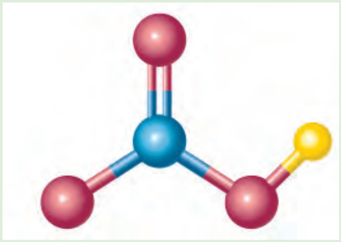
ISBN 978-99944-2-038-4

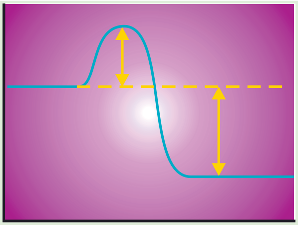
Contents

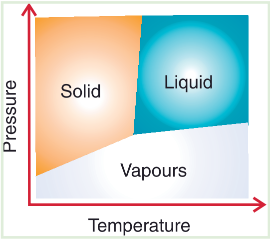
Page

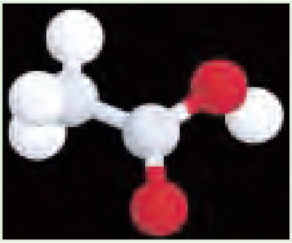




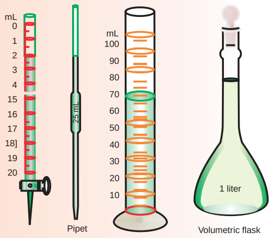





Pressure
Solid
Liquid
Vapours
Temperature



UNIT 1



Fundamental Concepts in Chemistry

Unit Outcomes

At the end of this unit, you should be able to:

- *understand the scope of chemistry;*
- *select and use appropriate SI units;*
- *understand the causes of uncertainty in measurement;*
- *express the result of any calculation involving experimental data to the appropriate number of decimal places or significant figures;*
- *use scientific methods in solving problems;*
- *demonstrate an understanding of experimental skills in chemistry;*
- *demonstrate a knowledge of laboratory procedures; and*
- *demonstrate scientific enquiry skills including observing, inferring, predicting, comparing and contrasting, communicating, analyzing, classifying, applying, theorizing, measuring, asking questions, developing hypotheses, performing and designing experiments, interpreting data, drawing conclusions, making generalizations and problem solving.*

MAIN CONTENTS

1.1 The Scope of Chemistry
  - Definition of Chemistry
  - Major Branches of Chemistry

1.2 Measurements and Units in Chemistry
  - SI Units: Basic and Derived
  - Prefixes used in SI Units
  - Uncertainty in Measurement
  - Precision and Accuracy
  - Decimal Places
  - Significant Figures
  - Scientific Notation

1.3 Chemistry as Experimental Science
  - Scientific Method
  - Experimental Skills in Chemistry
  - Writing a Laboratory Report

Start-up Activity

Form a group and collect as many objects as possible available to you like pen, paper, lunchbox, chalk, mobile phone, belt, towel, etc. Now, discuss the following questions and share your ideas with rest of the class.

1. Are all the objects made up of the same material? Try to classify them as plastic, leather, metal, wood, paper, etc.

2. Do these objects have the same use? Do they have multiple usages?
3. How would you decide which object is more appropriate for a particular use?
4. Can you use these objects at all temperatures?
5. What properties do you look for in a material for a particular use?
6. Are all the objects biodegradable?

Extend your discussion to describe the extent to which chemistry is used to understand matter and our environment.

INTRODUCTION

People in the industrialized nations enjoy not only the highest standard of living, that is, the material comforts which are measured by the goods, services and luxuries available to an individual, but also quality life. Quality life depends upon business and employment, services, health and nutrition, population, leisure time in addition to standard of living. Much of this is due to chemistry.

Chemistry enables us to design all sorts of materials: drugs to fight diseases; pesticides to protect crops and our health; fertilizers to grow abundant food; fuel for transportation; fibres to provide comfort and variety in clothes; building materials for housing; plastics for diverse uses; and much more.

When we address ourselves the most fundamental question: *What is the nature of life*? Chemistry provides essential information on this subject. The theories of chemistry illuminate our understanding of the material world from tiny atoms to giant polymers.

Everything you see, smell, taste and touch is made up of matter. Even the way you perceive the world through your senses involves chemical reactions. With such an enormous range of topics, it is necessary to know about chemistry in order to understand the world around us.

Figure: 1.1 Chemistry in everyday life.

Almost everything around us involves chemistry. The world around us consists of compounds made of various elements. Human body consists mainly of carbon, oxygen and hydrogen. Our environmental issues like global warming, ozone layer depletion, acid rain, etc., also require understanding of the fundamentals of chemistry.

1.1 THE SCOPE OF CHEMISTRY

At the end of this section, you should be able to:

- define chemistry;
- distingiuish the major fields of chemistry; and
- distinguish the sub-divisions of the branches of chemistry.

1.1.1 Definition of Chemistry

Activity 1.1

Form a group and enlist the activities you perform daily such as brushing your teeth, getting ready for school, enjoying your meals, studying in the school, playing, off to bed etc.

Now, discuss the following questions and share your ideas with rest of the class.

1. What is your tooth brush, toothpaste and soap made of?
2. Why do soaps have a cleansing action?
3. What makes petrol/CNG (compressed natural gas) a better fuel than wood?
4. Is it possible to use wires made of rubber for conduction of electricity?
5. What properties of cement, iron and stone make them suitable for construction of houses, etc. but not for making an aircraft?
6. Why metals like gold and silver are preferred for making jewellery?
7. Why is it necessary to cook certain food items?

Chemistry is the science that deals with matter and the changes that it undergoes. It is a study of the composition, structure, and properties of matter and of the changes that occur in matter.

Perhaps the only permanent thing in the world is change. Iron rusts, snow melts, paints peel off and firewoods burn. We grow up, we grow old. Living plants and animals undergo ceaseless change, and even dead animals and plants continue to change as they decay. Such changes fascinated people and inspired them to look more closely at nature's way of working.

Understanding change is closely related to understanding the nature and composition of matter- the physical material of the universe. Matter is anything that occupies space and has mass.

It has long been known that matter can change or be made to change from one form to another. These changes are broadly classified into chemical and physical changes. Chemical changes, more commonly called as chemical reactions are processes whereby one substance is transformed into another as a result of combination or dissociation of atoms. We can describe the transformation both qualitatively and quantitatively with the help of chemical equations for the reaction. Some of the examples of chemical change include oxidation of matter (*rusting, burning*), fermentation, changing milk in to yogurt, and addition of water to calcium oxide.

Matter also undergoes other kinds of changes called physical changes. These changes differ from chemical reactions in that the involved substances do not change their identities. Each retains its composition. Most physical changes are accompanied by changes in physical state, such as the melting of solids and the boiling of liquids. For example, water remains H_2O whether it is in solid state (*ice*), liquid water or gaseous state (*steam*). Physical change also involves making or separating mixtures. Dissolving table salt (NaCl) in water is a physical change.

There are two kinds of physical properties, namely, extensive and intensive physical properties.

Extensive physical properties are the properties, which depend on the amount or quantity of sample and therefore, can vary from sample to sample. The extensive property of a piece of copper wire, for instance, includes its length, diameter, mass, and electrical resistance.

Intensive physical properties are properties which do not depend on the amount of a substance present. The intensive properties of a piece of copper wire include its density, colour, melting point, and hardness. Intensive properties are useful in distinguishing between different substances because they do not vary from sample to sample.

Exercise 1.1

1. How do physical and chemical changes differ?
2. Classify the following properties of a piece of copper foil into extensive and intensive physical property:
    - Thickness
    - Conductivity
    - Solubility
    - freezing point
    - Smell (odour)
    - Area
    - Specific gravity
    - Weight of a substance
3. Describe importance of chemistry with the help of examples.

1.1.2 Major Fields of Chemistry

The universe is just like a very big chemical laboratory, rearranging atoms and sub-atomic particles to produce elements and compounds. While planets are made up of rocks which are nothing but arrangement of compounds, an atmosphere is a mixture of compounds separated by distance.

Since chemistry is such an enormous area of science, for convenience it has been divided into disciplines. However, the division is never as clear-cut as it might appear to be. All sciences are related and depend on each other – they are interrelated.

All the disciplines of science share information and methods with each other. For example, biology uses the findings of both physics and chemistry to study living organisms. Chemistry utilizes the information gathered by physics about the nature of matter and energy to study the properties and interactions of substances.

There are several branches of chemistry, the major branches are, Inorganic chemistry, Organic chemistry, Physical chemistry and Analytical chemistry.

- **Inorganic chemistry** is the study of all the elements and their compounds with the exception of carbon and its compounds (which falls under the category of organic chemistry). It investigates the characteristics of substances that are not organic, such as nonliving matter and minerals found in the earth's crust. Oxides, sulphides and carbonates form the important classes of inorganic compounds.

- **Organic chemistry** is the chemistry of carbon compounds except carbides, cyanides, carbon dioxide, carbon monoxide, carbonates and hydrogen carbonates. Perhaps the most remarkable feature of organic chemistry is that it is the chemistry of carbon and a few other elements, chiefly, hydrogen, oxygen, nitrogen, halogens and sulphur. The major nutrients in the food comprises of organic compounds such as carbohydrates, proteins, fats, vitamins, etc.

- **Physical chemistry** is the study of physical properties of materials, such as their thermal, electrical and magnetic behaviour and their interaction with electromagnetic fields. A chemical system can be studied from either a microscopic or a macroscopic point of view. The microscopic point of view makes explicit use of the concept of molecules. The macroscopic point of view studies large-scale properties of matter without explicit use of the molecule concept. Some important divisions of physical chemistry are thermodynamics, spectroscopy, quantum chemistry, chemical kinetics and electrochemistry.

- **Analytical chemistry** is a branch of chemistry which is concerned with the development of theoretical foundations and methods of chemical analyses. It involves separating, identifying and determining the relative amount of components in a sample of material. Chemical analysis may be qualitative or quantitative. Qualitative analysis reveals the chemical identity of the species in the sample while quantitative analysis establishes the relative amount of one or more of these species in numeric terms.

There is yet another important branch of chemistry, which bridges chemistry and biology, known as biochemistry. It involves the study of the science of the molecules and chemical reactions of life, and utilizes the principles and language of chemistry to explain biology at the molecular level.

Activity 1.2

Form a group and perform the following activities:

1. Investigate the ways in which the major areas of chemistry are further subdivided. You can use reference books and the internet to augment your current ideas.
2. Discuss the principles of chemistry involved in the daily-life and share your ideas with the rest of the class.

Exercise 1.2

1. Are the three states of matter inter-convertible? What type of change will it be?
2. Classical, alchemical, medical and technological traditions were chemistry's forerunners. Identify the contributions which each of these made to the development of chemistry.

1.2 MEASUREMENTS AND UNITS IN CHEMISTRY

At the end of this section, you should be able to:

- list and describe the seven SI units and their prefixes;
- write the names and symbols of derived SI units;
- use the factor-label method for solving problems and conversion to SI units;
- describe uncertainty of measurement;
- identify the digits that are certain and the ones that are uncertain given a number representing a measurement;
- identify the causes of uncertainity in measurement;
- define precision and accuracy;
- estimate the precision that is possible for any instrument, you use in the laboratory;
- explain system errors and random errors;
- analyze the given data in terms of precision and accuracy;
- define decimal places;
- determine the number of decimal places in a calculated result;
- define significant figures;
- determine the number of significant figures in a calculated result; and
- use scientific notation in writing very large or very small numbers.

1.2.1 SI Units (The International System of Unit)

In order to test a hypothesis, a scientist must gather data by measurement. Before the hypothesis is accepted, other scientists must reproduce the measured data. Data gathering and checking are much easier to accomplish if all scientists agree to use a common system of measurement. The system that has been agreed upon since 1960 is the international system of units (Système International d'Unités). The System International is a set of units and notations that are standard in science. It is a modernized version of the metric system that was established in France in 1795.

A unit of measurement is a definite magnitude of a physical quantity (mass, length, temperature, etc.) that has been chosen as the standard against which other measurements of the same physical quantity are made. For example, metre is the unit of measurement for length in the metric system.

All measurements consist of two parts: a scalar (numerical) quantity and the unit designation. For example, when an object is 2 metres long, it means that the object is two times as long as the unit standard (1 metre). In this example, the scalar quantity is 2 and the unit designation is metre.

Basic SI Units

In chemistry, two systems of units were commonly used for expressing the fundamental physical quantities such as mass, time, and length. They are:

- The cgs system – centimetre-gram-second
- The mks system – metre-kilogram-second

In the cgs system, the basic unit of length is centimetre (cm), mass is gram (g), and of time is second (s). In the mks system, the basic unit of length is metre (m), of mass kilogram (kg), and of time is second (s). In this way, each system defines individual base units for each of the fundamental physical quantities. All measured quantities can be expressed in terms of the seven base units listed in Table 1.1.

Table 1.1 The seven SI base units

Physical Quantity	SI Base unit	Symbol of unit
Mass	kilogram	kg
Length	metre	m
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	Cd

From these seven base units, all except candela, are relevant to chemistry.

Activity 1.3

Form a group and perform the following activity.

Take a small piece of magnesium ribbon. Measure its mass and length. Now put it in 20 mL of dilute hydrochloric acid and measure the time required for magnesium ribbon to dissolve completely. Record the temperature of solution before and after putting the magnesium ribbon in it.

Discuss the following questions:

1. What instruments/equipments did you use for measuring the physical quantities?
2. What units did you use to express them?
3. What is the difference between the physical quantities, namely mass and length?
4. Which is the appropriate unit to express the time taken for the above reaction to go to completion?
5. Explain the difference between heat and temperature.
6. Which basic SI units are appropriate to express the:
   a length of a race track,
   b average room temperature, and
   c time duration for the earth to have one rotation around its axis?

i) *Mass*

Mass of an object is the amount of matter present in it. It is measured with an analytical balance and in contrast to weight, mass is not affected by gravity.

ii) *Length*

The SI base unit of length is the metre (m). To measure length much larger than the metre, we often use the kilometre (km).

In the laboratory, lengths smaller than a metre are often most convenient. For example, the centimetre (cm) and the millimetre (mm).

On the submicroscopic scale, the micrometre (μm), the nanometre (nm), etc., are used.

iii) Time

The SI base unit for measuring intervals of time is the second (s). Short times are expressed through the usual SI prefixes: milliseconds (ms), microseconds (μs), nanoseconds (ns), and picoseconds (ps). Long time intervals, on the other hand, are usually expressed in traditional, non – SI units: minute (min), hour (h), day (d), and year (y).

iv) Temperature

Temperature is a measure of the average energy of motion or kinetic energy, of a single particle in a system. The instrument for measuring temperature is called thermometer. From common experience, we know that if two objects at different temperatures are brought together, heat flows from the warmer to the colder object. For example, if you touch a hot test tube, heat will flow from the test tube to your hand. If the test tube is hot enough, your hand will get burned. The temperature of the warmer object drops and that of the colder object increases, until finally the two objects are at the same temperature (thermal equilibrium). Temperature is therefore a property that tells us in what direction heat flows.

The SI basic unit of temperature is the Kelvin (K). For most routine laboratory work, we can use a more familiar temperature scale: the Celsius scale. On this temperature scale, the freezing point of water is 0°C, and its boiling point is 100°C. Another temperature scale, probably unfamiliar to most people, is the Fahrenheit scale. The relationship between these three temperature scales is given below:

$$°\mathrm{C} = \frac{5}{9}(°\mathrm{F} - 32)$$

$$°\mathrm{F} = \frac{9}{5}°\mathrm{C} + 32$$

$$\mathrm{K} = °\mathrm{C} + 273.15$$

The unit for temperature in the Kelvin scale is Kelvin (K, NOT k!).

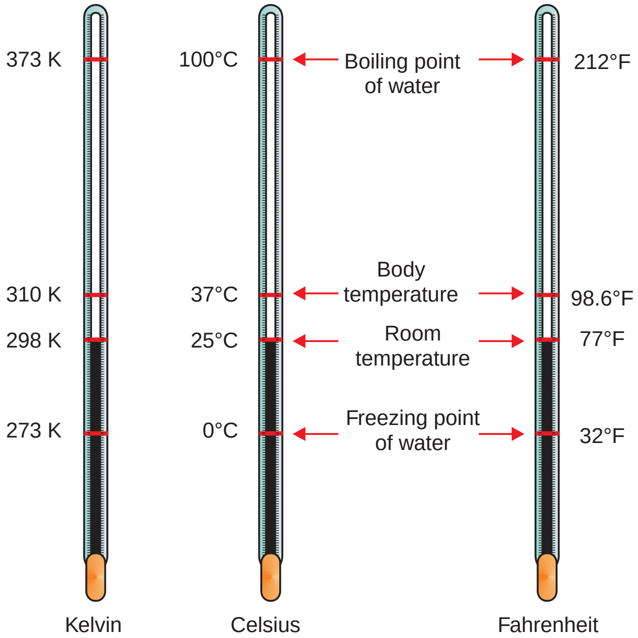


Figure1.2 The three temperature scales.

Activity 1.4

Form a group and describe the difference between mass and weight.

Share your ideas with the class.

The Kelvin scale assigns a value of zero Kelvin (0K) to the lowest possible temperature, which is called absolute zero and corresponds to –273.15°C. Note that the term absolute zero is used because this is a hypothetical temperature characterized by complete absence of thermal (kinetic) energy.

v) Mole (Amount of Substance): A mole of any substance (atoms, molecules or ions) represents 6.023×10^{23} particles of that substance. This number is also known as Avagadro's constant (N_o)

Exercise 1.3

1. The average temperature in Addis Ababa, during the summer, is about 25°C. What is the equivalent Kelvin temperature?
2. A parasite that causes trichinosis is killed when meat is cooked to 66°C. Assume you have only a Fahrenheit thermometer. Determine the minimum Fahrenheit temperature to which the meat should be heated when it is being cooked.

Derived SI Units

People often say that gold is "heavy" and aluminium is "light". Do they mean that a gold bracelet weighs more than an aluminium extension ladder?

Derived physical quantities are expressed in derived SI units. Although units used to express derived physical quantities are actually derived from basic SI units, they are often given special names for convenience. For example, force, volume, density, concentration, pressure, area, energy, etc., are derived quantities.

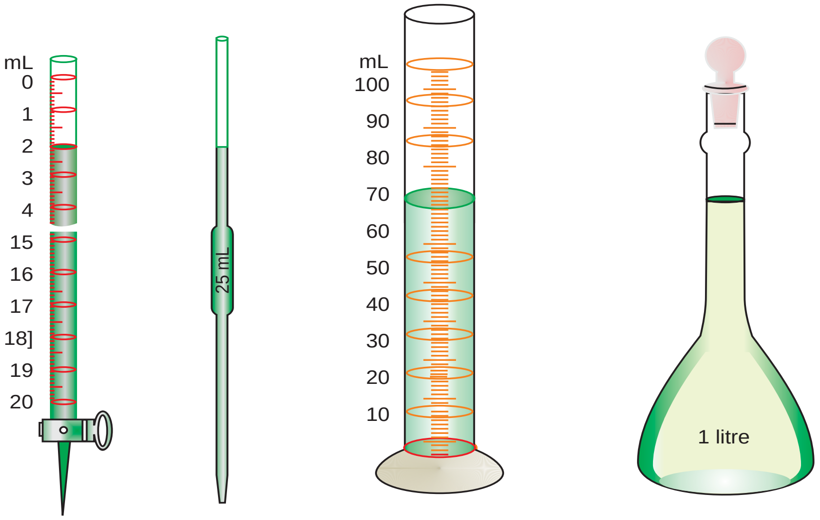
i *Force* is the product of mass and acceleration.

$$\begin{aligned} \text{Force} &= \text{mass} \times \text{acceleration} \\ &= \text{kg} \times \text{m/s}^2 = \text{kg m s}^{-2} \end{aligned}$$

Therefore, kilogram–metre per second squared is the SI unit of force. This combination of units is called the Newton (N).

$$1 \text{ N} = 1 \text{ kg m s}^{-2}$$

ii *Volume* is the amount of space occupied by a solid, liquid or gas. The volume of a liquid can be measured by using graduated (measuring) cylinder, a burette, or a pipette while a volumetric flask is used to take measured volume of the liquid.



Burette (*a*) Pipette (*b*) Measuring cylinder (*c*) Volumetric flask (*d*)

Figure 1.3 Some commonly used measuring apparatus.

Volume is a derived quantity in chemistry, so it is given a special unit, the litre (L). In SI units, one litre is defined as being equal to 1000 cubic centimetres (cm^3).

$$1L = 1000\ cm^3$$

$$1mL = 1\ cm^3$$

$$1L = 1\ dm^3$$

so, $$1000\ cm^3 = 1dm^3$$

The volume of a solid object with a rectangular shape can be calculated as:

$$\text{Volume} = \text{length} \times \text{width} \times \text{height}$$

iii *Density* is the amount of mass in a unit volume of matter. Its symbol is ρ.

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \quad \text{or} \quad \rho = \frac{m}{v}$$

Density can be measured in units of $g\ cm^{-3}$, $kg\ m^{-3}$ or g/mL.

For example, 1.00 g of water occupies a volume of 1.00 cm^3 or 1 mL.

$$\rho = \frac{m}{v} = \frac{1.00\,g}{1.00\,cm^3} = 1.00\ g\ cm^{-3}$$

It may be noted that the density of a substance is always measured at specific temperatures.

Example 1.1

Aluminium has a density of 2.70 $g\ cm^{-3}$. What is the mass of a piece of aluminium with a volume of 0.525 cm^3?

Solution:

Since $\rho = m/V$, it follows that $m = \rho \times V$

$$m = 2.70\ g\ \cancel{cm^{-3}} \times 0.525\ \cancel{cm^{-3}}$$

$$= 1.42\ g$$

Exercise 1.4

1. Ethanol is used in alcoholic beverages and has a density of 0.789 g/mL. What volume of ethanol (in litres) would have a mass of 500 g?
2. Calculate the density of a rectangular block of metal whose length is 8.335 cm, width is 1.02 cm, height is 0.982 cm and mass is 62.3538 g.
3. A piece of silver metal weighing 194.3 g is placed in a graduated cylinder containing 242.0 mL of water. The volume of water now reads 260.5 mL. Calculate the density of the metal.
4. Oil floats on the surface of water but mercury sinks. Explain why.

iv *Concentration*: The concentration of a solution is the amount of solute present in a given quantity of solvent or solution.

For many practical applications, the concentrations of solutions are expressed in molarity, molality and mole fraction.

Can you predict the base unit for concentration from those derived units of concentration?

For example, the molarity of a solution relates an amount of solute in moles (mol) and a solution volume in cubic decimetres (dm^3), or the amount of solute in moles (mol) and solution volume in litres (L).

$$\text{Concentration in molarity} = \frac{\text{number of moles of solute}}{\text{volume in litre of solution}}$$

Units of molarity: mol dm^{-3} and mol L^{-1}.

v Pressure is defined as force per unit area over which the force is exerted.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

Thus, the SI unit of pressure is Newton per metre square (N m^{-2}). This unit is called Pascal (Pa) (in honour of Blaise Pascal who investigated the effect of pressure on fluids).

1 Pascal (1 Pa) = 1 Newton per metre square (1 N m^{-2}).

Frequently used non-SI units for expressing pressure are millimetre of mercury (mmHg), torr, and atmosphere (atm).

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr} = 101.3 \text{ kPa}$$

1.2.2 Common Prefixes Used in SI Units

Activity 1.5

Form a group and discuss the following:

Why would it be difficult to use kilograms to express the amounts of chemicals used in large-scale industrial quantities and the amounts of chemicals used for laboratory experiments?

After the discussion, share your ideas with the rest of the class.

We use prefixes to indicate decimal multiples or fractions of the base units. The international system uses a series of prefixes to indicate decimal fractions or multiples of various units by powers of 10. All numbers can be expressed in the form of $a \times 10^b$, where 'a' is a number between 1 and 10, and the exponent 'b' is an integer. This feature makes it easy to convert from one unit to another. Some of the most commonly encountered prefixes in chemistry are listed in Table 1.2.

Table 1.2 Some common SI prefixes

Prefix	Meaning	Symbol	Multiple/Fraction
tera	trillion	T	10^{12}
giga	billion	G	10^{9}
mega	million	M	10^{6}
kilo	thousand	k	10^{3}
deci	tenths of	d	10^{-1}
centi	hundredth of	c	10^{-2}
milli	thousandth of	m	10^{-3}
micro	millionth of	μ	10^{-6}
nano	billionth of	n	10^{-9}
pico	trillionth of	p	10^{-12}

When we solve numerical problems, we use an approach to units called dimensional analysis. Dimensional analysis was developed to ensure that our answers yield proper units. It also offers a systematic approach to solve numerical problems and check our solutions for possible errors.

In dimensional analysis, we carry units through all calculations. As we work, we multiply units together, divide them by each other, and 'cancel' them.

The key to use dimensional analysis is the correct use of conversion factors in order to change one unit into another. A conversion factor is a fraction whose numerator and denominator are the same physical quantity expressed in different units. For example, 100 cm and 1 m are the same length, 100 cm = 1 m. This relationship allows us to write two conversion factors:

$$\frac{100\ \text{cm}}{1\ \text{m}} \quad \text{and} \quad \frac{1\ \text{m}}{100\ \text{cm}}$$

The first of these factors is used when we want to convert metres to centimetres and second centimetres to metres. For example, the length in centimetres of an object that is 8.50 m long is given by:

desired unit

$$\text{Number of centimetres} = 8.50\ \text{m} \times \frac{100\ \text{cm}}{1\ \text{m}} = 850\ \text{cm}$$

given unit

Note that the unit of metre in the denominator of the conversion factor cancels the unit of metre in the measurement given (8.50 m). The centimetre in the numerator of the conversion factor becomes the unit of the final answer. In general, the units multiply and divide as follows:

$$\cancel{\text{given}}\ \cancel{\text{unit}} \times \frac{\text{desired unit}}{\cancel{\text{given}}\ \cancel{\text{unit}}} = \text{desired unit}$$

If the desired units are not obtained in a calculation, then we know that we made an error somewhere. Careful inspection of units often reveals the source of the error.

Exercise 1.5

1. If a man has a mass of 115 pounds, what is his mass in grams (1 lb = 453.6 g)?
2. A piece of aluminium foil is 8.0×10^{-5} cm thick. What is its thickness in micrometres?
3. Convert 75 ng to mg.
4. Convert 6.75 m^3 to μL.
5. Convert each of the following measurements to a unit that replaces the power of ten by a prefix.
   - a 3.22×10^{-6} s
   - b 9.56×10^{-3} m
   - c 1.07×10^{3} g
6. Calcualte the mass in grams of two cubic inches (2.00 in^3) of gold. Density of gold = 19.3 g cm^{-3}.

1.2.3 Uncertainty in Measurements

In scientific work, we recognize two kinds of numbers: exact numbers (whose values are known exactly) and inexact numbers (whose values have some uncertainty).

Exact numbers are those that have defined values or are integers that result from counting number of objects. For example, by definition, there are exactly 12 eggs in a dozen and exactly 1000 g in a kilogram. The number one is any conversion factor between units, as in 1m = 100 cm, of course the number one is also an exact number.

Numbers obtained by measurement are always inexact. Uncertainties always exist in measured quantities. There are many causes of uncertainty, but the most important are usually

- the person doing the measurement,
- the measuring device,
- the environment where the measurement is being made, and
- variability in the item being measured.

Making a measurement usually involves comparing the item you are measuring with a unit or a scale of units. It is often impossible to obtain the exact value of the quantity measured, unless all the numbers are exact integers.

Activity 1.6

Form a group and perform the following activities.

1. Make a chain of paper clips or other objects of uniform length. Then use a metre stick to measure a series of lengths on the chain. For example, measure sections containing one, two, three, etc., clips. Record your results and share them with your classmates.
2. Using laboratory scale, take several mass reading for one, two, three objects of uniform size. You can use any convenient objects you find in the laboratory. Record your results and discuss them in your group. Focus especially on the similarities and differences in your measurement. Did you all find the same reading for the same object? What do you think are the cause of the uncertainties, if any?

Discuss the results with the rest of the class.

1.2.4 Precision and Accuracy in Measurements

Precision and accuracy are terms which are used to express uncertainties in measurement. Precision is a measure of how clearly individual measurements agree with one another. Accuracy refers to how closely individual measurements agree with the correct or 'true' value.

Activity 1.7

Form a group, perform the following activities and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

A laboratory instructor has given a sample of amino acid powder to four students, A, B, C and D. Each student is asked to weigh the sample and record his/her results. The true (accepted) value is 8.72 g. Their results for three trials are:

Trials	Student A	Student B	Student C	Student D
1	8.72 g	8.50 g	8.50 g	8.41 g
2	8.74 g	8.77 g	8.48 g	8.72 g
3	8.70 g	8.83 g	8.51 g	8.55 g

a Calculate the average mass from each set of data, and determine which set is the most accurate.

b Which set of data is the most precise? Is this set also the most accurate?

c Which set of data is the least accurate? Is this set also the least precise?

A possible set of results obtained from a measurement of the length of a table with a metre stick by five students is given in Table 1.3.

Table 1.3 A set of measurements of length

Student	Length (m)
1	2.157
2	2.150
3	2.153
4	2.159
5	2.156
Average	2.155

The precision of a set of measurements refers to the degree of reproducibility among the set. The precision is good (or *high*) if each of the measurements is close to the average of the series. The precision is low (or *poor*) if there is a wide deviation from the average value. The precision of the data in Table 1.3 is good. Each measurement is within 0.005 m of the average value. In contrast the accuracy of a set of measurement refers to the closeness of the average of the set to the ‘‘correct’’ or ‘‘true’’ value.

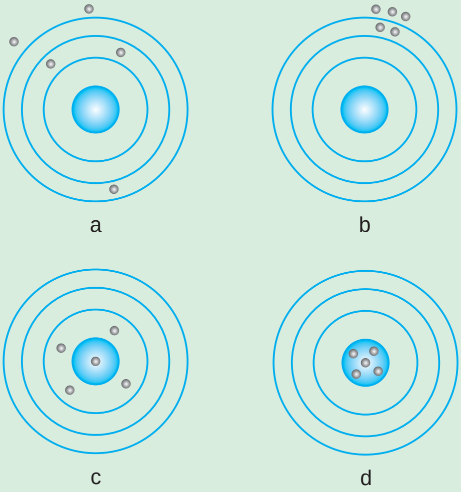
Measurements of high precision are more likely to be accurate than are those of poor precision, but even highly precise measurements are sometimes inaccurate.

Example 1.2

Four persons A, B, C and D used targets a, b, c and d respectively while practicing with a rifle. The results are illustrated in Figure 1.4. How do you explain the following results?

a Target a represents low accuracy and low precision.
b Target b represents low accuracy and high precision.
c Target c represents high accuracy and low precision.
d Target d represents high accuracy and high precision.

Read the figure’s legend and tally with your answers.



(The central blue region is the centre of the target)

a measurements of low accuracy and low precision are scattered and off-centre;
b those with low accuracy and high precision form a tight off-centre cluster;
c those with high accuracy and low precision are evenly distributed but are distant from the centre; and
d those with high accuracy and high precision are bunched in the centre of the target.

Figure 1.4 Comparing precision and accuracy.

Exercise 1.6

Four students measured the mass of a piece of metal whose accurate mass is 34.75 g. Their results are 34.2 g, 33.75 g, 35.0 g, and 34.69 g.

a What is the best estimate for the mass of the piece of metal? Explain why?

b Explain whether the results are precise or accurate?

The precision of a result is a measure of the certainty of the value. Usually the result is quoted as a plus-or-minus (±) value. For example, the accepted value of a universal gas constant (R) is 8.314 J mol^{-1} K^{-1}. One student might quote a result of (8.34 ± 0.03) J mol^{-1} K^{-1}, while another student gives a value of (8.513 ± 0.0006) J mol^{-1} K^{-1}. The result of the former student is more accurate (*i.e., closer to the true* (*accepted*) *value*), while that of the latter student is the more precise (*i.e., has the smallest uncertainty*).

Precision and accuracy are linked with two common types of errors called Random and Systematic errors.

Random error makes a measurement less precise but not in any particular direction. In other words, the actual value may be either greater or smaller than the value one records. Random errors arise mostly from inadequacies or limitations in the instrument. On the other hand this may be a result of how precisely someone can read a metre or a scale.

For example, consider the measuring cylinder shown in Figure 1.3c; we would probably take the reading as 70.0, but in doing so, we say that it is nearer to 70.0 than it is to 69.9 or 70.1. In other words, it is greater than 69.95 (had it been less we would have recorded it as 69.9) and smaller than 70.05 (had it been greater we would have recorded it as 70.1); hence, we should record this value as 70.0 ± 0.05.

In some cases, such as many thermometers, it is only possible to read a scale to the nearest 0.2 (that is, one would record 28.0, 28.2, 28.4, 28.6, etc., but never an odd final digit such as 28.3, 28.5, 28.7 etc.). In this case, the uncertainty would be ± 0.1, because a reading of 28.2 means it is greater than 28.0, but less than 28.4.

Systematic errors produce values that are either entirely higher or smaller than the actual value. It always affects a result in a particular direction, and skews the accuracy of the experiment in that direction. Systematic errors arise from flaws or defects in the instrument or from errors in the manner that the measurement was taken.

For example, when you are taking the initial reading of a burette that is placed well above head height, you might decide to read the top rather than the bottom of the meniscus. Systematic errors can lead to inconsistent results.

Exercise 1.7

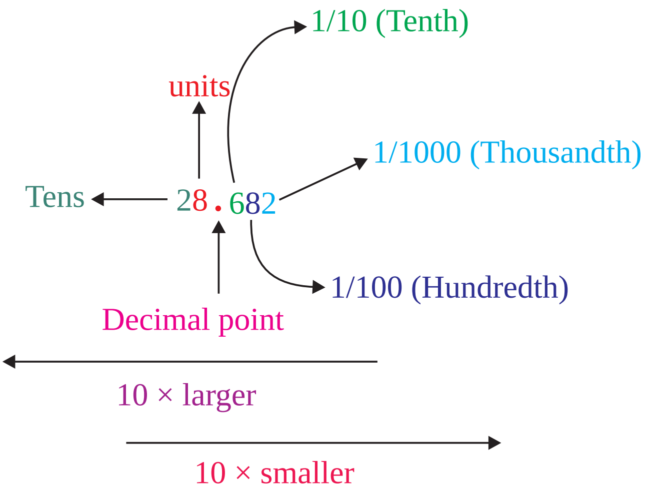
Indicate which of the following allow you to give exact numbers when you measure them:

a The mass of a paper clip;
b The surface area of a coin;
c The number of inches in a mile;
d The number of ounce in a pound;
e The number of microseconds in a week;
f The number of pages in this text book.

1.2.5 Decimal Places

A decimal place refers to the number of digits to the right of the decimal point. Each successive position to the right of a decimal point has denominator increased by a power of ten. For example, 0.087 is a number given to three decimal places, and in 0.087, 0 is the first decimal place, 8 is the second, 7 is the third.

A point or dot (•) used to separate the whole number part from the fractional part of a number is called a decimal point.



To express a value to the n^{th} decimal place, look at the values of the $(n + 1)^{th}$ digit, as stated in the following rules.

1 If the $(n + 1)^{th}$ digit is 4 or less, leave the n^{th} digit unchanged. For instance, 369.648 rounds to 369.6 if we want one decimal place.

2 If $(n + 1)^{th}$ digit is greater than 5 round up the n^{th} digit. For instance, 936.758 can be rounded to 936.76 if we want to express the result upto two decimal places.

3 If the digit to be removed is 5, the preceding number increases by one unit if it is odd and remains unchanged if it is even. For example, 17.75 rounds to 17.8, but 17.65 rounds to 17.6. Note that if 5 is followed only by zeros, the left-most digit is unchanged. But if the 5 is followed by non-zeros, the final digit is increased by 1. For example, 17.6500 rounds to 17.6, but 17.6513 rounds to 17.7.

Example 1.3

1. Round 7.1284 to 2 decimal places.
2. Round 0.1284 to 1 decimal place.
3. Round 26.895 to 2 decimal places.

Solution:

1. The 3^{rd} decimal number, 8, is bigger than 5, so we add 1 to the 2^{nd} decimal number, 2, and drop the rest of the decimal numbers. Our answer is 7.13.
2. The 2^{nd} decimal number, 2, is less than 5, so we do nothing to the 1 and we drop the rest of the decimal numbers. Our answer is 0.1.
3. The second decimal number, 9, is odd, so we add 1 to 9 to get 10, and drop the rest of the decimal numbers. But, we have to carry the 1 to the 8 to get 9. So our answer is 26.90 or just 26.9.

1.2.6 Significant Figures

Significant figures are those digits that correctly indicate the precision of a measurement. So significant figures show both the limits of accuracy and where the uncertainty begins. For this reason, it is important to indicate the margin of error in measurement by clearly indicating the number of significant figures, which are the meaningful digits in a measured or calculated quantity.

It may be noted that measurements that were taken by the five students in Table 1.3 agree on the first three digits (2.15); they differ only in the fourth digit. The last digit in a scientific measurement is usually regarded as uncertain. All digits known with certainty, plus one of uncertain value, are called significant figures.

The measurements in Table 1.3 have four significant figures. In other words, we are quite sure that the length of the table is between 2.15 m and 2.16 m. Our best estimate, including the uncertain digit, is the average value, i.e., 2.155 m.

The last digit in a significant figure is uncertain because it reflects the limit of accuracy.

The following guidelines apply to determining the number of significant figures in a measured quantity. It has to be decided whether zeros are significant in three different situations.

1. If the zeros precede the first non-zero digit, they are not significant. Such zeros merely locate the decimal point. *i.e.*, they define the magnitude of measurement. For example, 0.004 m has one significant figure, and 0.00016 m has two significant figures.
2. If the zeros are between non-zero digits, they are significant. For example, 204408 kg has six significant figures while 0.05504 has four significant figures.
3. If the zeros follow non-zero digits, there is ambiguity if no decimal point is given. For example, if a volume is given as 200 cm^3, there is no way of expressing if the final two zeros are significant. But if the volume is given as 200 cm^3, zeros after a non-zero digit preceded by a decimal point make all figures significant. Thus, 200.cm^3 has three significant figures. If it is given as 200.0 cm^3, it has four significant figures.
4. Non-zero digits are always significant.

Example 1.4

1. How many significant figures are there in:

   a 0.0004802 b 6, 834 c 5, 2100

2. A calculator display shows the result of a calculation to be 67340.468. How many significant figures are there?

Solution:

1. a four significant figures
   b four significant figures
   c ambiguous
2. Eight significant figures.

1.2.7 Scientific Notation

The ambiguity in significant figures can be avoided by expressing the measurements in scientific notation. Scientific notation is a way of expressing large or small numbers as factors of the powers of 10. The exponents of 10 can be used to make the expression of scientific measurements more compact, easier to understand, and simpler to manipulate. For example, the mass of an electron is 0.000 000 000 000 000 000 000 000 000 91 g, and the value of Avogadro's number is 602, 000, 000, 000, 000, 000, 000, 000 mol^{-1}. In scientific notation, these values can be expressed as 9.1×10^{-28} g and 6.02×10^{23} mol^{-1} respectively.

To express numbers in scientific notation, you use the form $a \times 10^b$, where a is a decimal number between 1 and 10 (*but not equal to 10*), and is known as the digit term, and b is a positive or negative integer or zero and is called the exponent.

To express a number in scientific notation, count the number of places you must move the decimal point in order to get '*a*' between 1 and 10. Moving the decimal point to the right (*if the number is less than 1*) indicates a negative exponent, and moving the decimal point to the left (*if the number is greater than 1*) indicates a positive exponent.

Example 1.5

Express the following numbers in scientific notation (each with three significant figures)

a 7500000 b 0.000777

Solution:

a 7.50×10^6 b 7.77×10^{-4}

Exercise 1.8

1. Express 0.0000000013 in scientific notation.
2. Express each of the following with the number of significant figures indicated:
   a 5,000.083 (to three significant figures)
   b 3,986.0 (to four significant figures)

Follow the following rules for proper answers of the results of substraction, addition, multiplication, and division of numerical values.

1. For addition and subtraction, the answer should contain no more digits to the right of the decimal point than any individual quantity. i.e., use the least number of decimal places.
2. For multiplication and division, a result can only be as accurate as the factor with the least number of significant figures that goes into its calculation. i.e., use the least number of significant figures.

Example 1.6

1. What is the area, in square metres, of a room that is 12.42 m long and 4.81 m wide?
2. Perform the following calculation and round off the answer to the correct number of digits.

$$49.146 + 72.13 - 9.1434 = ?$$

Solution:

1. The length of the room is expressed to four significant figures and the width to three. By whatever method we use to carry out the multiplication, we are limited to three significant figures in our answer.

$$12.42 \text{ m} \times 4.81 \text{ m} = 59.7 \text{ m}^2$$

2. In this calculation, we must add two numbers and, from their sum, subtract the third. We express the answer to two decimal places, the number of decimal places in '72.13'. We do this in two ways below:

a

$$\begin{array}{r} 49.146 \\ +\,72.13 \\ \hline 121.276 \end{array} = \begin{array}{r} 121.28 \\ -9.1434 \\ \hline 112.1366 \end{array} = 112.14$$

b

$$\begin{array}{r} 49.146 \\ +72.13 \\ \hline 121.276 \\ -\,9.1434 \\ \hline 112.1326 \end{array} = 112.13$$

The preferred method is b, where we do not round off the intermediate result: 121.276.

Exercise 1.9

1. Perform the indicated operations and give answers with the proper number of digits.
   - a 451 g – 15.46 g – 20.3 g
   - b 15.436 L + 5.3 L – 6.24 L – 8.177 L
   - c 48.2 m + 3.82 m + 48.4394 m
   - d 148 g + 2.39 g + 0.0124 g
   - e 37 m × 2.340 m × 0.52 m
   - f 62.89 m ÷ 4.7 m
2. The distance between carbon atoms in a diamond is 154 pm. Convert this distance to millimetres.
3. In a certain part of the country, there is an average of 710 people per square mile and 0.72 internet services per person. What is the average number of internet services in an area of 5.0 km^2?

1.3 CHEMISTRY AS EXPERIMENTAL SCIENCE

At the end of this section, you should be able to:

- define scientific method;
- describe the major steps of the scientific method;
- use scientific methods in solving problems;
- demonstrate some experimental skills in chemistry; and
- describe the procedures of writing laboratory reports.

1.3.1 The Scientific Method

Activity 1.8

Form a group and perform the following activity.:

- a Collect a pastic bag filled with different items provided by your teacher.
- b Decide on the question you would like to answer about your bag. Write it down. (Do not open the bag)
- c Guess what the answer to your question might be. Write down. (Do not open the bag)
- d Open your bag and answer the questions.

e Be sure to count the total number of items.

Now, discuss which part of the activity (a, b, c, d, or e) introduces the scientific terminology: hypothesis, data collection, experimentation, etc.

Discuss the results with the rest of the class.

Science is an organized body of knowledge that is based on a method of looking at the world. The scientific methods are unique, and require any explanation of what is seen to be based on the results of experiments and observations. These experiments and observations must be verifiable by anyone who has the time and means needed to reproduce them.

Although two different scientists rarely approach the same problem in exactly the same way, there are guidelines for the practice of science that have come to be known as the scientific method. These guidelines are outlined in Figure 1.5.

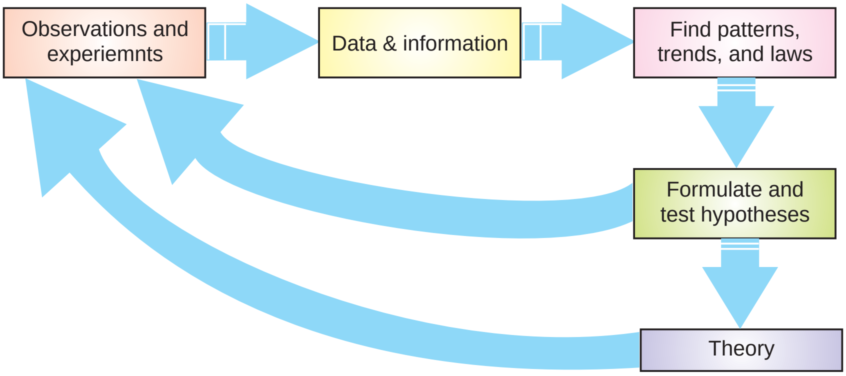


Figure1.5 Steps in scientific methods.

The scientific method is a general approach to problems. It involves making observations, collecting information/data, seeking patterns in the observations, formulating hypothesis to explain the observations, and testing these hypothesis by further experiments. If a hypothesis successfully posses many tests, it becomes a theory, which is a tested explanation of a hypothesis.

Activity 1.9

Form a group and imagine/enact that you are a group of scientists who have discovered a new chemical compound of great use in curing cancer.

1. How would you present your work to other scientists of the world?
2. Is there a particular format to write scientific reports?

   Discuss the essential features of a well-designed experiment.
3. Consider the following:
   - a Strike a match stick to light it.
   - b Record all your observations in writing.
   - c Examine your written observations and consider their objectivity.

   Which of these do you think are just descriptions of your observations?

   In contrast, which are the ideas that you formed based on your observations?

   Finally, which of your data could be subjective or partly subjective? Why?

Present your observations to your classmates. As you do so, describe the objectivity or subjectivity of each statement that you make. In particular, discuss those that you inferred based on observation.

Scientists seek general relations that unify their observations. A concise verbal statement or a mathematical equation that summarizes a broad variety of observations and experience is known as scientific law. A familiar example is the law of gravity. It summarizes the experience that what goes up must come down.

Scientists also seek to understand laws. A tentative explanation of a law is called a hypothesis. A hypothesis is useful if it can be used to make predictions that can be tested by further experiments and can thereby be verified.

A hypothesis that continually withstands such tests is called a theory. A theory is an explanation of the general principles of certain phenomena that has considerable evidence or facts to support it. It may serve to unify a broad area and may provide a basis for explaining many laws.

There is no fool-proof, step-by-step scientific method that people use. Their approaches depend on their temperaments, circumstances and training. Rarely will two people approach the same problem in the same way. Scientific progress is not smooth, certain and predictable. The path of any scientific study is likely to be irregular and uncertain. Progress is often slow, and many promising leads turn out to be dead ends. Serendipity (*fortunate accidental discovery*) as well as perseverance has played an important role in the development of science.

1.3.2 Some Experimental Skills in Chemistry

Activity 1.10

Form a group and perform the following activities. Discuss the results with the rest of the class.

Consider the reaction between a copper wire and concentrated nitric acid. Observe this reaction and suggest possible solutions for the following questions:

Has the copper wire disappeared?

Have the copper atoms disappeared? If not disappeared, where are they?

What are the expected products?

Is this change physical or chemical?

Caution: The gaseous product formed is pungent, irritating and poisonous; do not inhale it and do not allow it to escape in the air.

Experimental Skills

Chemistry has two main roles in the curriculum. Chemistry is pre-requisite for many other courses in higher education, such as medicine, biological and environmental sciences. It is an experimental science that combines academic study with the acquisition of practical and investigatory skills in order to:

- plan experimental activity, i.e., planning;
- carry out experimental work, i.e., implementing;
- analyse and draw conclusions from the results of experimental work, i.e., analysing evidence and drawing conclusions; and
- evaluate the work, i.e., evaluating evidence and procedures.

To acquire these experimental skills and investigations you should be able to:

- follow a sequence of instructions;
- use techniques, apparatus and materials;
- make and record observations, measurements and estimates;
- interpret, evaluate and report upon observations and experimental results;
- design/plan an investigation, select techniques, apparatus and materials; and
- evaluate methods and suggest possible improvements.

It is not possible to prepare an exhaustive list of skills, but the major skills that are ideally developed in a laboratory environment include:

1. Skills in the safe handling of chemical materials, taking into account their physical and chemical properties, including any specific hazards associated with their use.
2. Skills required for conducting the standard laboratory procedures involved in synthetic and analytical work, in relation to both inorganic and organic systems.
3. Skills in monitoring, by observation and measurement, of chemical properties, events or changes, and the systematic and reliable recording and documentation thereof.
4. Competence in planning, design and execution of practical investigations, from the problem-recognition stage to the evaluation and appraisal of results and findings; this includes the ability to select appropriate techniques and procedures.
5. Skills in the operation of standard chemical instrumentation such as that used for structural investigations and separation.
6. Ability to interpret data derived from laboratory observations and measurements in terms of their significance and the theory underlying them.
7. Ability to conduct risk assessments concerning the use of chemical substances and laboratory procedures.

Chemistry Laboratory Apparatus

Laboratory equipment comprises different sets of apparatus, which are designed to perform various tasks in the laboratory. On the basis of their use, these apparatus can be broadly classified into three categories:

1. Reaction vessels, *e.g.*, Beakers, flasks, boiling tubes and test tubes.
2. Measuring equipments, *e.g.*, Pippetes, burettes, balances and thermometers.
3. Support and heating devices, *e.g*. Stand and clamp, tripod and gauze, spirit burner and Bunsen burner.

The practical activities are intended to support conceptual development. Proficiency in handling of apparatus is the result of continual practice.

Note: The information about care and safety associated with the use of some of these apparatus/devices have been discussed at various places in this unit. However, adequate information about these is obtained when these are actually used to perform experiments in the laboratory or elsewhere.

Chemistry Laboratory Safety Rules

The chemistry laboratory may be considered as a place of discovery and learning. However, by the very nature of laboratory work, it can be a place of danger if proper common-sense precautions are not taken. It is your duty in law to take reasonable care for your own health and safety and that of others working in the laboratory. Therefore, it is essential that the students are taught what can go wrong, how to prevent such events from occurring, and what to do in case of an emergency.

Protect your eyes

- Appropriate eye protection must be worn at all times! Inform your teacher if you wear contact lenses.

Wear appropriate protective clothing

- Your clothing should cover your legs to the knees; shorts are not appropriate for the laboratory. Loose clothing should not be worn because it may dip into chemicals or fall into a flame and catch fire. Further, laboratory aprons can be used to protect your clothing.

Wear shoes that cover your feet

- Due to the dangers of broken glass and corrosive liquid spills in the laboratory, open sandals or bare feet are not permitted in the laboratory. Remember! leather shoes protect your feet from chemical spills – canvas shoes do not.

Tie back loose hair

- Dangling hair can fall into the Bunsen burner and catch fire or can fall into a chemical solution

Eating and drinking in the laboratory

- Do not taste any chemical! Even food, drink and chewing gum are prohibited in the chemistry laboratory. These activities are ways by which you can accidentally ingest harmful chemicals

Smelling chemicals

- Do not smell any chemicals directly!
- Smell chemicals only if your teacher specifically tells you to do so, then use your hand to fan the vapour towards your nose.

Pipetteing out solutions

- Do not suck the solutions in the pipette by mouth!
- Use a rubber suction bulb (pipette bulb) or other device to fill a pipette.

General precautions

- Wash your hands with soap and water before leaving the laboratory even if you have been wearing gloves.
- Know the hazards of the materials being used.
- When lighting the Bunsen burner, first light the match stick then turn on the gas.
- Know how to interpret data from a MSDS (Material Safety Data Sheets).
- Read the labels on the reagent bottles carefully to make sure that you are using the right chemical.

- Never add water to concentrated acid solutions. The heat generated may cause spattering. Instead, as you stir, add the acid slowly to water.
- Hold your hand over the label while pouring.
- For minor skin burns, immediately plunge the burned portion into cold water and inform the teacher.
- If you get any chemical in your eye, immediately wash the eye with the eye-wash fountain and notify the teacher.
- Work with volatile chemicals under a fume hood.
- Never look directly into a test tube. View the contents from the side.
- Get acquainted with the location and proper usage of the safety equipments like eye wash fountain, safety shower, fire extinguisher, emergency exits.
- Carry out only the experiments assigned by your teacher.
- Use equipment only as directed.
- Never place chemicals directly on the pan balances.
- Use glycerin when inserting glass tubing into rubber stoppers.
- Be cautious of glassware that has been heated. Handle hot glassware with gloves or beaker tongs.
- Add boiling chips to liquid to be boiled.
- Point test tubes that are being heated away from you and others.
- Check glassware for stars or cracks.
- Never use laboratory glassware for eating or drinking purposes.
- Never remove chemicals from the laboratory.
- Never work alone in the laboratory. In case of a problem, you may need another person to prevent injury or even save your life!

Demonstrate safe behaviour

- Obey all safety instructions given by your teacher or found in you experimental procedure.

- Clean up spills immediately if you know. If you are uncertain how to clean up a spill or if a large spill occurs, notify your teacher immediately.
- Before leaving the lab be sure to replace the lids to all containers, return equipment and chemicals to their proper places and clean up your work area.
- Know how to dispose off waste. Dispose off all waste materials according to your instructional procedure or your teacher's instructions.
- Remember that the lab is a place for serious work! Careless behavior may endanger yourself and others and will not be tolerated!
- Know how to respond to an emergency.
- Report any accidents or unsafe conditions immediately!
- For some experiments, it may be helpful to anticipate data. You should always read the experiment in advance.

Note: Additional safety precautions will be announced in class prior to experiments where a potential danger exists.

1.3.3 Writing a Laboratory Report

The purpose of writing an introductory laboratory experiment is to give practice in writing laboratory reports that answer the general questions:

- What did you do?
- Why did you do it?
- How did you do it?
- What happened?

A laboratory report is a written composition of the results of an experiment. It should be written precisely and clearly, using good grammar and punctuation. Each report must include: title, objective, materials and (equipment) used, procedure, observation, result, discussion, and conclusion.

1. *Title*: Create a title in less than ten words that reflects the factual content of your report

2. *Objective*: This section states the purpose of your experiment. Be specific about the outcomes that you plan to achieve when you designed your experiment.
3. *Materials used*: Describe the substances, equipment and instrumentation that is to be used in your work. Copy the format for this section from your laboratory manual or from the standard procedure supplied by the teacher.
4. *Procedure*: Describe how you performed the experiment, and mention each step in chronological order.
5. *Data/Observations*: This section demonstrates that you carried out an experiment carefully and knowledgeably. The person reading your report should find it clear and convincing enough to take your experimental results seriously.
6. *Result and Discussion*: In this section of the report, present your results and discuss them. Also report possible errors in the procedure and results, including possible inaccuracies.

   Include any problems that you encountered during your work. Present them objectively. If possible suggest ways in which such problems could be reduced at least if not overcome.
7. *Conclusion*: This section should be brief, as it refers back to the objectives and considers how and to what degree they have been met. Review the purpose of the experiment, and summarize the implications of the results.

Unit Summary

- The science of chemistry deals with the composition, physical properties, and chemical properties of matter.
- Matter is made up of atoms and molecules.
- All matter fits into two categories: substances and mixtures.
- The SI system has seven base units, six of which are used in chemistry.
- Some measurements are expressed directly in terms of base units as well as multiples or submultiples of a base unit. For example, you might express a length in metres as well as in kilometres or millimetres.

- A measured quantity must be expressed with the proper number of significant figures to indicate its precision.
- In reporting calculated quantities special attention must be paid to the concept of significant figures.
- Calculations can be done by the unit-conversion method.
- Techniques of estimating answers are also useful in problem solving.
- The scientific method involves making observations, doing experiments forming hypothesis, gathering data, and formulating laws and theories.

Check List

Key terms of the unit

- *Accuracy*
- *Analytical chemistry*
- *Basic unit*
- *Derived unit*
- *Extensive*
- *Hypothesis*
- *Inorganic chemistry*
- *Intensive*
- *Law*
- *Organic chemistry*
- *Physical chemistry*
- *Precision*
- *Scientific method*
- *Scientific notation*
- *Significant figure*
- *Theory*
- *Uncertainty*

Review Exercise

Part I: Multiple Choice Type Questions

1. Which of the following numbers has five significant figures?
   a 61,530 b 0.6153 c 0.006154 d 615.40
2. What is the mass of 30.0 mL of a liquid that has a density of 1.60 g/mL?
   a 18.8 g b 48.0 g c 31.6 g d 53.3 g

3. A blood sample analysis showed a total of 0.00361 g lead. Express it in micrograms?
   a 0.361 μg
   b 3.61×10^{3} μg
   c 3.61×10^{6} μg
   d 3.61×10^{4} μg
4. Which of the following statements is correct?
   a One metre has about the same length as a yard.
   b A scientific notation for 0.00035 is 3.5×10^{-3}.
   c A substance with a density of 0.80 g/cm^{3} sinks in water.
   d The prefix mega- means multiplied by 1,000,000.
5. A conversion factor, like the definition 100 cm = 1 m, is:
   a approximate
   b exact
   c cannot be predicted
   d subject to individual opinion
6. Which of the following is an extensive physical property?
   a colour
   b density
   c mass
   d melting point
7. The product of 12.76 cm and 0.0030 cm has __________ significant figures.
   a 2
   b 3
   c 4
   d 5
8. A measurement gave a mass of 0.45 kg. This is the same as:
   a 4.5 g
   b 45 g
   c 450 g
   d 4,500 g
9. Which of the following statements is not correct?
   a Density has no units.
   b Every measurement has a unit tied to it.
   c Physical quantities are properties that can be measured.
   d The kelvin degree is larger than the celsius degree.
10. The number 52.415 ± 0.0001 has ___________ significant figures.
    a 4
    b 5
    c 6
    d 7

Part II: Answer the following questions.

1. Convert – 40°C to °F.
2. Round off 45.68 metres to one decimal place.
3. How many seconds are there in 8 minutes?
4. Change each of the following measurements to one in which the unit has an appropriate SI prefix.

a 3.76×10^{3} m

b 6.34×10^{-6} g

c 1.09×10^{-9} g

5. How many significant figures are there in each of the following measured quantities?

a 4.200×10^{5} s c 6.02×10^{23} e 0.00075 m

b 0.1050 °C d 0.049300 g f 8008 m

6. Express each of the following measured quantities in exponential notation. Assume all the zeros in parts c and d, are significant.

a 0.00090 cm b 20.00 s c 9,000 s d 2,800 m

7. Perform the indicated operations and give answers with the proper number of significant figures.

a 48.2 m + 3.82 m + 48.4394 m

b 451 g – 15.46 g

c 15.44 mL – 9.1 mL + 105 mL

d $73.0 \times 1.340 \times 0.41$

e $\dfrac{22.61 \times 0.0587}{135 \times 28}$

8. A 25.0 mL sample of liquid bromine weighs 78.0 g. Calculate the density of the bromine.

9. Some metal chips with a total volume of 3.29 cm^{3} are placed on a piece of paper and weighed. The combined mass is found to be 18.43 g, and the paper itself weighs 1.2140 g. Calculate the density of the metal to the proper number of significant figures.

10. A rectangular block of lead is 1.20 cm × 2.41 cm × 1.80 cm, and it has a mass of 59.01 g. Calculate the density of lead.

11. A block of lead, with dimensions 2.0 dm × 8.0 cm × 35 mm, has a mass of 6.356 kg. Calculate the density of lead in g cm^{-3}.

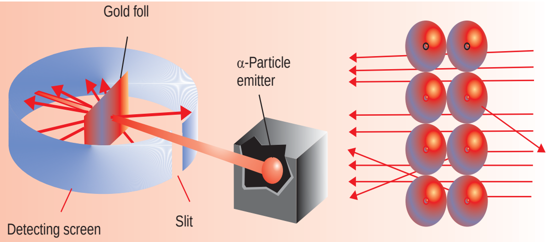
12. Demonstrate that kg L^{-1} and g cm^{-3} are equivalent units of density.

13. Steam is sometimes used to melt ice. Is the resulting change physical or chemical?

14. Which of the following lengths is the shortest and which is the longest? 1583 cm, 0.0128 km, 17931 mm, and 14 m

15. Which SI unit can be used for expressing the height of your classroom ceiling?

UNIT 2



Atomic Structure and the Periodic Table

Unit Outcomes

At the end of this unit, you should be able to:

- *understand the historical development of atomic structure;*
- *explain the experimental observations and inferences made by some famous scientists to characterize the atom;*
- *list and describe the subatomic particles;*
- *explain the terms "atomic mass" and "isotope";*
- *understand electromagnetic radiation, atomic spectra and Bohr's models of the atom;*
- *do calculations involving atomic structure;*
- *describe the quantum mechanical model of the atom, related postulates and principles;*
- *demonstrate an understanding of periodic law and how electronic configuration of atoms are related to the orbital diagrams and can explain periodic trends; and*
- *describe scientific inquiry skills along this unit: inferring, predicting, classifying, comparing, and contrasting, communicating, asking questions and making generalizations.*

MAIN CONTENTS

2.8 Electronic Configurations and the Periodic Table of the Elements
  - The Modern Periodic Table
  - Classification of the Elements
  - Periodic Properties
  - Advantages of Periodic Classification of the Elements

Start-up Activity

Form a group and try to explore the basic building blocks of the following:

a proteins,

b steel, and

c paper.

Why is it important to understand the properties of different types of matter?

After the discussion in your group, share your findings with the rest of the class.

2.1 HISTORICAL DEVELOPMENT OF THE ATOMIC NATURE OF SUBSTANCES

At the end of this section, you should be able to:

- State briefly the historical development of atomic nature of substances.

Activity 2.1

1. Form a group and try to find the smallest constituent of following materials: table salt, paper, sand, wood etc.
2. Discuss the following questions:
   a What is matter made up of?
   b Are all atoms similar in structure?
   c When and how were these atoms discovered?

d Can we see atoms with our naked eyes?

e How small are these atoms?

f Are atoms indivisible?

Share your ideas with rest of the class.:

This section will help us to get an understanding of the electronic structure of the atoms. A great deal of our understanding of electronic structure has come from studies of the properties of light or radiant energy. We begin our study by considering the historical development of the atomic nature of substances, and then we will learn how the atomic theories were developed.

A theory of the structure and behaviour of atoms has taken more than two millennia to evolve, from ancient Greek philosophers to the high-tech experiments of modern scientists. Prior to the scientific revolution and the development of the scientific method, starting in the 16th century, ideas about the atom were mainly speculative. It was not until the very end of the 19th century that technology became advanced enough to allow scientists a glimpse of the atom's constituent parts: the electron, proton and neutron.

Activity 2.2

In your Grade 9 chemistry lesson, you have learned about historical development of the atomic nature of substances.

1. Form a group and discuss on the belief of ancient Greek philosophers about the atomic nature of substances. Present your group discussion report to the class.
2. Refer to different chemistry reference books and, in group, discuss on how the beliefs about the structure of matter evolved. Start from early historical developments.

2.2 DALTON'S ATOMIC THEORY AND THE MODERN ATOMIC THEORY

At the end of this section, you should be able to:

- state postulates of Dalton's atomic theory;
- state postulates of Modern atomic theory; and

- state the laws of conservation of mass, definite proportions, multiple proportions and the basis of each of these laws.

Activity 2.3

Form a group and do the following activity:

Take 1g of iron fillings and 1.75g of sulphur powder. Heat them strongly to form a new compound iron (II) sulphide. Weigh the new compound formed.

NOTE: Perform the activity under the guidance of your teacher.

Discuss the following questions and share your findings with the rest of the class.

1. What is the weight of new compound formed?
2. Can we create or destroy mass?
3. Is there any fixed ratio in which elements combine?
4. What are the laws of chemical combination?
5. Will the molecular formula of the synthesized iron (II) sulphide be same as that available in the laboratory?

In Grade 9, you learned about Dalton's and Modern Atomic Theories. Here again you will spend some more time on these theories.

2.2.1 Postulates of Dalton's Atomic Theory

Scientific laws usually develop based on previous scientific findings. The laws that are the basis for Dalton's atomic theory are the law of conservation of mass and the law of definite proportions.

What is the law that Dalton formulated based on these two laws and write its statement in your notebook? Illustrate this law using C and O to form CO.

Example 2.1

1. A nitrogen-oxygen compound is found to have an oxygen-to-nitrogen mass ratio of 1.142 g oxygen for every 1.000 g of nitrogen. Which of the following oxygen-to-nitrogen mass ratio(s) is/are possible for different nitrogen-oxygen compound(s)?

   a 2.285
   c 0.571
   b 1.000
   d 2.500

2. Determine, which of the following oxygen-to-nitrogen mass ratio(s) is/are also possible for nitrogen-oxygen compound. (Refer Example 2.1 No. 1 for required information)

   a 0.612
   c 1.713
   b 1.250
   d 2.856

Solution :

1. The given compound has 1.142 g of oxygen and 1.000 g of nitrogen. Response (a) has 2.285 g of oxygen for the same 1.000 g of nitrogen. The ratio of the masses of oxygen, 2.285:1.142, is almost exactly 2:1. Response (a) seems to be correct possibility, so is response (c). Here the ratio is 0.571:1.142 = 0.500 = 1:2.

   Responses (b) and (d) are not possibilities. They yield ratios of 1.000:1.142 = 0.875 and 2.500: 1.142 = 2.189, respectively. Neither of these can be expressed as a ratio of small whole numbers.

2. By the same method,

   a 0.612:1.142 = 0.536:1 is not possible
   b 1.250:1.142 = 1.095:1 is not possible
   c 1.713:1.142 = 1.5:1 or 3:2, is possible
   d 2.856:1.142 = 2.5:1 or 5:2 is possible

Activity 2.4

In your Grade 9 chemistry lesson, you have learned about the laws of conservation of masss and the law of definite proportion. Form a group and discuss the following statements. Share your ideas with the rest of the class.

1. The mass of a piece of wood before and after it is burnt to ashes is not the same, showing that mass can be created or destroyed. Is it a violation of law of conservation of mass?

   What would be the mass of products if the burning of wood was carried out in a closed container?
2. Sugar consists of C, H, and O atoms. When a certain amount of sugar is burned in a crucible, nothing remains in the crucible. Have the carbon, hydrogen and oxygen atoms of the sugar been destroyed? If so, how? If not, where have they disappeared?
3. A sample of sodium chloride from Afar contains the same percent by mass of sodium as one from Tigray.
4. Arsenic and oxygen can combine to form one compound, which is 65.2% by mass arsenic, and another compound, which is 75.8% by mass arsenic.

Exercise 2.1

1. List the postulates of Dalton that continue to have significance (are retained in modern atomic theory).
2. Match the atomic theory statements in part A with the matching items in part B.

	Part A		Part B
I	All matter is composed of extremely small, indivisible particles called atoms.	a	Although graphite and diamond have different properties (due the nature of interatomic bonding) they are composed only of carbon. The carbon atoms are identical.
II	All atoms of a given element are identical in mass and other properties, but atoms of one element differ from the atoms of every other element.	b	$2H_2 + O_2 \rightarrow 2H_2O$, not CS_2 or NaCl.
III	Atoms are not created, destroyed or converted into other kinds of atoms during chemical reactions. They are simply rearranged into new compounds.	c	There are 6.02×10^{23} atoms in 55.85 g of iron.

3. How does the atomic theory account for the fact that when 1.00 g of water is decomposed into its elements, 0.111 g of hydrogen and 0.889 g of oxygen are obtained regardless of the source of the water?
4. Hydrogen peroxide is composed of two elements: hydrogen and oxygen. In an experiment, 1.250 g of hydrogen peroxide is fully decomposed into its elements.
   a If 0.074 g of hydrogen are obtained in this experiment, how many grams of oxygen must be obtained?
   b Which fundamental law does this experiment demonstrate?
   c How is this law explained by the atomic theory?
5. A 15.20 g of nitrogen will react with 17.37 g, 34.74 g, or 43.43 g of oxygen to form three different compounds.
   a Calculate the mass of oxygen per gram of nitrogen in each compound.
   b How do the numbers in part (a) support the atomic theory?

2.2.2 Postulates of Modern Atomic Theory

Activity 2.5

Form a group and discuss the following questions:

Which of Dalton's postulates about atoms are inconsistent with later observations?

Do these inconsistencies mean that Dalton was wrong? Is Dalton's model still useful?

Share your ideas with the rest of the class.

Most of the experiments conducted during the development of the modern atomic theory will be presented and explained in Sections 2.3 - 2.6. In this section, generalizations derived from the experiments are presented as postulates of modern atomic theory.

Modern atomic theory is generally said to begin with John Dalton. Dalton's work was mainly about the chemistry of atoms – how they combine to form new compounds – rather than about the internal structure of atoms. However, Dalton never denied the possibility of atoms having a structure. Modern theories about the physical structure of atoms did not begin until J.J. Thomson discovered the electron in 1897.

In 1913, a Danish physicist, Niels Bohr, who had studied under both Thomson and Rutherford, further modified the nuclear model. He proposed that electrons move only in restricted, successive shells and that the valence electrons determine the chemical properties of different elements. In the 1920s, Bohr's theory became the basis for quantum mechanics, which explained in greater detail the complex structure and behaviour of atoms.

Activity 2.6

Form a group and discuss the following questions:

1. Describe the limitations of Dalton's Atomic Theory.
2. Write the postuates of Modern Atomic Theory.

Share your discussion with the rest of the class.

2.2.3 How the Modern Theory Explains the Mass Laws

Activity 2.7

Form a group; use your Grade 9 knowledge and discuss the modern atomic theory to explain the:

a law of conservation of mass

b law of definite proportions and

c law of multiple proportions.

Share your discussion with the rest of the class.

Chemical compounds are formed when atoms combine in whole-number ratios (*law of multiple proportions*). A given compound always has the same relative number and types of atoms (*law of constant composition*).

In a chemical reaction, the mass of the reactants (*starting materials*) equals the mass of the reaction products (*law of conservation of mass*), provided no reactant remains.

2.3 EARLY EXPERIMENTS TO CHARACTERIZE THE ATOM

At the end of this section, you should be able to:

- discuss the discovery of the electron;
- describe the properties of cathode rays;
- define the terms: radioactivity, radioactive decay and radio-isotope;
- describe the common types of radioactive emissions;
- discuss the alpha scattering experiment; and
- describe the major contribution of experiments by Thomson, Millikan and Rutherford concerning atomic structure.

2.3.1 Discovery of the Electron

Historical Note

Sir Joseph Thomson

J. J. Thomson (1856-1940) was a British physicist and Nobel laureate. Sir Joseph John Thomson was born near Manchester, England, and educated at Owens College (now part of Victoria University of Manchester) and Trinity College, University of Cambridge. At Cambridge he taught mathematics and physics, served as Cavendish Professor of Experimental Physics, and was (1918-40) master of Trinity College. He was also president of the Royal Society (1915-20) and professor of natural philosophy at the Royal Institute of Great Britain (1905-18).

Thomson was awarded the 1906 Nobel Prize in physics for his work on the conduction of electricity through gases. He is considered the discoverer of the electron through his experiments on the stream of particles (electrons) emitted by cathode rays. A theorist as well as an experimenter, in 1898, Thomson advanced the "plum-pudding" theory of atomic structure, holding that negative electrons were like plums embedded in a pudding of positive matter. Thomson was knighted in 1908.

Cathode Rays

In 1879, the English scientist William Crookes (1832-1919) experimented with gas-discharge tubes. When a very high electrical potential (~ 10,000 volts) is applied across a gas taken in a discharge tube of a very low pressure (~ 0.001 torr) some radiations are emitted from cathode. These radiations are called cathode rays. Fig 2.1, shows emission of cathode rays in a discharge tube. At this stage the glass walls of the discharge tube opposite to the cathode starts glowing with a faint greenish light. It is now known that this greenish glow on the walls is due to the bombardment of the glass wall with the cathode rays.

Cathode rays normally travel in straight lines, but are deflected when a magnet is brought nearby (Figure 2.1b).

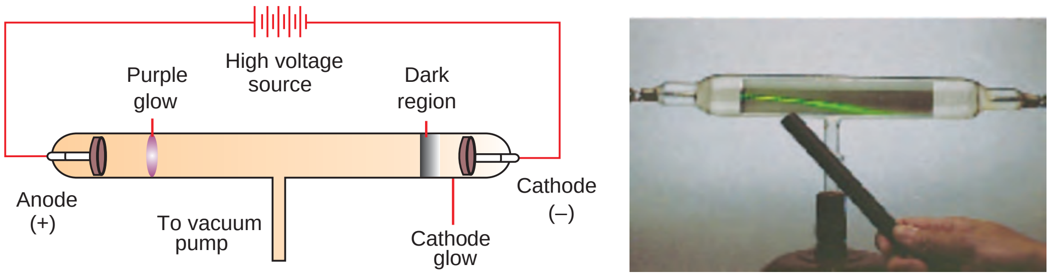


Figure 2.1 (a) Electric discharge in an evacuated tube. **(b) The cathode ray is bent in the presence of a magnet.**

An English physicist Joseph John Thomson (1856-1940) in 1897 studied the behaviour of cathode rays in electric and magnetic fields, Thomson established clearly that the rays consist of negatively-charged particles. Moreover, his experiments showed that the particles were identical, regardless of the materials from which the electrodes were made or the type of gas in the tube. Thomson concluded that these negatively charged particles were constituents of every kind of atom. We now call these particles electrons, a term that had been coined by the Irish Physicist George Stoney in 1891 to describe the smallest unit of electric charge. Cathode rays are beams of electrons.

Perhaps Thomson's most significant experiment was the one illustrated and described in Figure 2.2. By measuring the amount of deflection of a cathode ray beam in electric and magnetic fields of known strengths, Thomson was able to calculate the ratio of the mass of an electron to its charge. If we denote the mass of the electron as m_e and its electrical charge as e, the mass-to-charge ration is m_e/e. This ratio has a value of -5.686×10^{-12} kg C^{-1} (kilograms per coulomb).

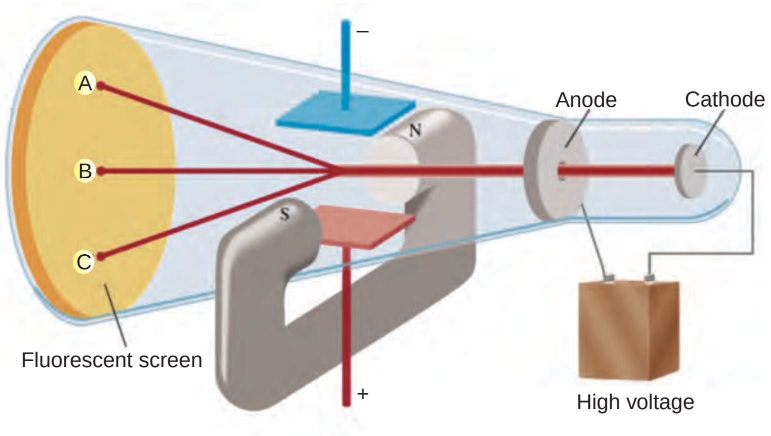


Figure 2.2 Thomson's apparatus for determining the charge-to-mass ratio.

In 1909, Robert A. Millikan, an American physicist, determined the charge on the electron by observing the behaviour of electrically-charged oil drops in an electric field. Based on careful experiments, Millikan established the charge on an electron as $e = -1.602 \times 10^{-19}$ C. From this value and the value for m_e/e, we can calculate the mass of an electron.

$$m_e = \frac{m_e}{e} \times e = -5.686 \times 10^{-12}\ \text{kg C}^{-1} \times -1.602 \times 10^{-19}\ \text{C}$$

$$= 9.109 \times 10^{-31}\ \text{kg}$$

In 1923, Millikan was awarded the Nobel Prize in physics for his oil-drop experiment.

2.3.2 Radioactivity and Discovery of Nucleus

Radioactivity

Radioactivity is the spontaneous emission of radiation from the unstable nuclei of certain isotopes. Isotopes that are radioactive are called radioactive isotopes or radioisotopes. For example,

$$^{55}_{24}\text{Cr},\ ^{226}_{88}\text{Ra},\ ^{14}_{6}\text{C},\ ^{238}_{92}\text{U},\ ^{14}_{7}\text{N}$$

are radioactive isotopes. Radioactive decay is defined as a nuclear breakdown in which particles or (electromagnetic) radiation is emitted. Shortly after the discovery of radioactivity, three types of rays were identified in the emanations from radioactive substances. One type called alpha (α) particles which consist of particles that have a mass that is about four times that of a hydrogen atom. They also have a charge twice the magnitude of an electron but positive rather than negative. An alpha particle is now known to be a doubly-ionized helium atom, that is, He^{2+}.

A second type of radiation was shown to consist of negatively-charged particles, identical to cathode rays. These particles are called beta (β) particles, which are electrons, coming from inside the nucleus.

The third type of radiation, called gamma (γ) rays, is a form of electromagnetic radiation much like the X-rays but of even higher energy. Like X-rays, but unlike alpha and beta particles, gamma rays are a form of energy and not a form of matter.

Activity 2.8

Form a group and do the following. Share your ideas with the rest of the class.

In your notebook, make a table of the three kinds of radiation you have read about. Use the given table headings for the types of radiation, response to magnetic field, mass and charge as follows. Then fill in the cells.

Types of radiation	Greek letter	Mass Number	Charge	Deflected

Discovery of Nucleus

In 1910, the New Zealand chemist and physicist, Ernest Rutherford, who had studied with J.J. Thomson decided to use α-particles to probe the structure of atoms. Together with his associate Hans Geiger, Rutherford carried out a series of experiments using very thin foils of gold and other metals as targets for α-particles from a radioactive source.

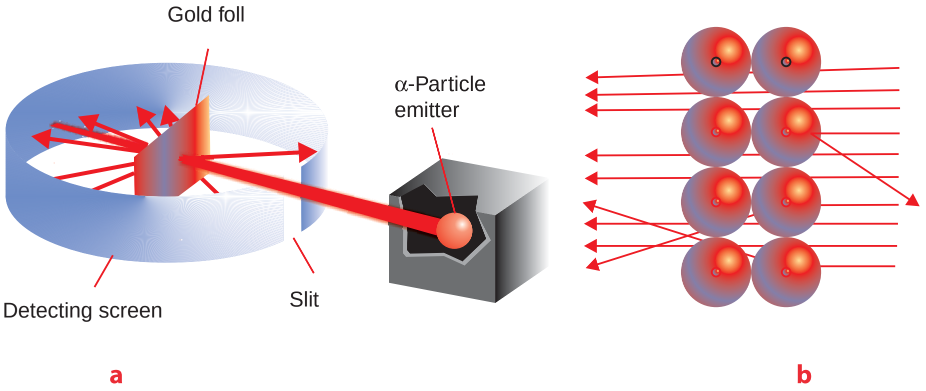


Figure 2.3 a Rutherford's experimental design for measuring the scattering of α-particles by a piece of gold foil.

b Magnified view of α-particles passing through and being deflected by the nucleus.

Activity 2.9

From a group and discuss Rutherford's experiment as shown in Figure 2.3 a and b answer the following questions:

1. Why majority of the α-particles penetrating the foil where undeflected?
2. Why small fraction of the α-particles showed slight deflection?
3. Why all α-particles did not bounced by an angle of 180°?
4. Based on the finding of Rutherford's experiment how will you conclude that most of the space in the atom is empty?
5. Which observation led to conclusion that all the positive charge in the atom is concentrated in the nucleus?

Report your findings to the class.

2.3.3 Discovery of Neutron

Except for the lightest hydrogen isotope, protium ($^{1}_{1}H$), atoms have more mass than is indicated by the numbers of their protons (*Before the 1930's, protons were considered as the sole contributors to the mass of an atom*). For example, a helium nucleus, with two protons has a mass four times that of hydrogen. If all the mass came from the protons, a helium atom would have only twice the mass of a hydrogen atom. The reason for this "*excess*" mass puzzled scientists for several years.

One hypothesis was that the atomic nucleus also contained electrically neutral fundamental particles.

In the 1920s and early 1930s, alpha particles were used as projectiles to bombard a variety of materials. Bombardment of beryllium atoms produced a strange, highly penetrating form of radiation. In 1932, James Chadwick (1891-1972) showed that this radiation was best explained as a beam of neutral particles. These particles, called *neutrons*, were found to have about the same mass as protons but no electric charge. This discovery finally provided an explanation for the mysterious excess mass. A helium atom has two protons and two neutrons. Because protons and neutrons have roughly the same mass (and *electrons have almost no mass*) the helium atom should have about four times the mass of the hydrogen atom. The mass of a neutron, $m_n = 1.67493 \times 10^{-27}$ kg, is about 1840 times the mass of electron.

2.4 MAKE UP OF THE NUCLEUS

At the end of this section, you should be able to:

- describe make-up of the nucleus;
- define atomic mass;
- define isotope; and
- calculate the relative atomic mass (atomic mass) of naturally occurring isotopic elements.

2.4.1 Constituents of the Nucleus

Activity 2.10

Form a group and complete the following table by drawing in your notebook. Discuss your ideas with the rest of the class.

Symbol	Atomic Number	Number of neutrons	Mass Number	Number of electrons
$^{12}_{6}C^{+}$	–	–	–	–
–	16	–	32	18
–	–	14	27	13
Pb	82	126	–	–

In 1914, Rutherford suggested that the smallest positive-ray particle was the fundamental unit of positive charge in all nuclei. He called this particle, which has a charge equal in magnitude but opposite in sign to that of an electron, a proton. A proton has a mass of $m_p = 1.67262 \times 10^{-27}$ kg, which is about 1840 times the mass of oppositely-charged electrons. Rutherford proposed that protons constitute the positively-charged matter in the nuclei of all atoms.

Table 2.1 The three subatomic particles

Particle	Symbol	Relative mass in atom	Approximate charge	Relative location
Proton	p^+	1	+1	Nucleus
Neutron	n°	1	0	Nucleus
Electron	e^-	0.000545	−1	Outside nucleus

To form the picture of an atom in your mind, think of it as something like this: if an entire atom were represented by a football field, the nucleus would be only about as big as a lentil located at the centre of the field.

2.4.2 Atomic Mass and Isotopes

Not all atoms of an element are identical in mass. All carbon atoms have six protons in the nucleus ($Z = 6$) but only 98.89 % of naturally occurring carbon atoms have six neutrons in the nucleus ($A = 12$). A small percentage (1.11 %) have seven neutrons in the nucleus ($A = 13$), and even fewer (less than 0.01 %) have eight ($A = 14$).

Most elements found in nature are mixtures of isotopes. The average mass for the atoms in an element is called the atomic mass of the element and can be obtained as averages over the relative masses of the isotopes of each element, weighted by their observed fractional abundances. If an element consists of n isotopes, of relative masses A_1, $A_2 \ldots A_n$ and fractional abundances of $f_1, f_2 \ldots f_n$, then the average relative atomic mass (A) of the element is:

$$A = A_1 f_1 + A_2 f_2 + \ldots + A_n f_n.$$

Activity 2.11

Form a group and discuss the following:

1. Are neutrons present in all atoms?

2. Can two atoms have the same number of electrons but different number of neutrons?
3. Can an atom have unequal number of electrons and protons?
4. Do the chemical properties of an atom depend on the number of electrons, protons or neutrons?
5. Why the atomic masses for most elements are not whole numbers?
6. Does an atom of zinc (Zn) have about the same mass as an atom of sulphur (S), about twice the mass, or about half the mass?
7. Nitrogen has two naturally occuring isotopes, N-14 and N-15. The atomic mass of nitrogen is 14.007 amu. Which isotope is more abundant in nature?

share your ideas with rest of the class.

Example 2.2

There are two isotopes of lithium found on earth. Isotope ^{6}Li (6.01512 m_u) accounts for 7.42% of the total, and isotope ^{7}Li (7.01600 m_u) accounts for the remaining 92.58%. What is the average atomic mass of lithium?

Solution:

$$\frac{7.42}{100} \times 6.01512\ m_u + \frac{92.58}{100} \times 7.01600\ m_u = 6.942\ m_u$$

Exercise 2.2

1. What is the mass number of an isotope of tin that has 66 neutrons and 50 protons?
2. Calculate the number of protons and neutrons for $^{24}_{12}Mg$ and $^{88}_{38}Sr$.
3. Why do isotopes of an element have similar chemical properties?
4. Element X is toxic to humans in high concentration but essential to life at low concentrations. Identify element X whose atoms contain 24 protons and write the symbol for the isotope with 28 neutrons.

5. Copper (Cu: atomic mass 63.546 m_u) contains the isotopes ^{63}Cu (mass = 62.9298 m_u) and ^{65}Cu (mass = 64.9278 m_u). What percent of a Cu atom is ^{65}Cu?
6. The element chlorine contains two isotopes: ^{35}Cl, which has a mass of 34.97 m_u, and ^{37}Cl, which has a mass of 36.97 m_u. Calculate the percentage of each chlorine isotope. The average atomic mass of chlorine is 35.5 m_u.
7. Carbon exists as the isotopes carbon-12, with a fractional abundance of 0.9890 and a mass of exactly 12 m_u, and carbon-13, with a fractional abundance of 0.0110 and a mass of 13.00335m_u. Calculate the average atomic mass of carbon.

2.5 ELECTROMAGNETIC RADIATION (EMR) AND ATOMIC SPECTRA

At the end of this section, you should be able to:

- characterize electromagnetic radiation (EMR) in terms of wave length, frequency and speed;
- calculate the wave length and frequency of EMR;
- explain that light has both wave and particle natures;
- define photon as a unit of light energy;
- explain how photon theory explains the photoelectric effect and the relationship between photons absorbed and electrons released;
- explain that emission spectra of atoms consist of series of lines;
- state Bohr's assumption of energy of electrons in the hydrogen atom;
- explain that the line spectrum of hydrogen demonstrates the quantized nature of the energy of its electron;
- explain that atoms emit or absorb energy when they undergo transition from one energy state to another;
- explain the shortcomings of the Bohr theory; and
- calculate the radius of an electron orbit, velocity and the energy of the electron, using the Bohr model.

2.5.1 Electromagnetic Radiation

Activity 2.12

Form groups and discuss on the following questions. Share your ideas with the rest of the class.

The nature of the nucleus has been known for quite some time - since the days of Rutherford and his associates. What has been illusive however is the position and velocity of electrons.

1. Is it possible to know the exact location of an electron? Defend your suggestion.
2. Do electrons have a particle nature or a wave nature?
3. Explain why an electron does not enter the nucleus even though they are oppositely charged?
4. What is the velocity of an electron?

In 1873, James Clerk Maxwell proposed that light consists of electromagnetic waves. According to his theory, an electromagnetic wave has an electric field component and a magnetic field component. Further, his theory accurately describes how energy, in the form of radiation, propagates through space as electric and magnetic fields. Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves.

The wave properties of electromagnetic radiation are described by two interdependent variables, frequency and wavelength. Wavelength (λ, *Greek lambda*) is the distance between any point on a wave and the corresponding point on the next wave; that is, the distance the wave travels during one cycle.

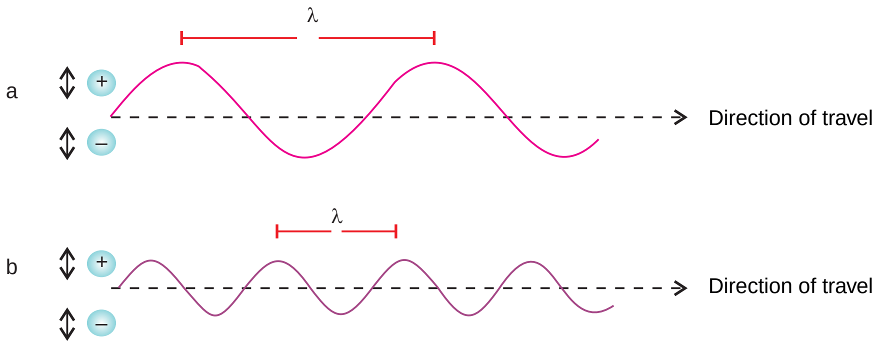


Figure 2.4 Electromagnetic waves.

In Figure 2.4, two waves with different wave lengths (λ) and thus different frequencies (ν) are shown. Wavelength is commonly expressed in meters, but since chemists often deal with very short wavelengths the nanometer, picometer and the angstrom are also used. Frequency (ν, Greek nu) is the number of cycles that pass a given point in space per second, expressed in units of s^{-1} or hertz (Hz).

The speed of the electromagnetic wave (light), *c* (distance travelled per unit time, in meters per second), is the product of its frequency (*cycles per second*) and its wavelength (*metres per cycle*),

$$c_0 = \nu \times \lambda \qquad \text{...(2.1)}$$

In vacuum, light travels at a speed of 2.99792458×10^8 m s^{-1} (3.00×10^8 m s^{-1} to three segnificant figures).

The speed of an electromagnetic wave depends on the nature of the medium through which the wave is travelling. The speed of an electromagnetic wave in medium (*c*) is the product of its wavelength and its frequency.

$$c = \lambda \times \nu \qquad \text{...(2.2)}$$

Another characteristic of a wave is its amplitude, the height of the crest (or depth of the trough) of the wave. The amplitude of an electromagnetic wave is a measure of the strength of its electric and magnetic fields. Thus, amplitude is related to the intensity of the radiation, which we perceive as brightness in the case of visible light.

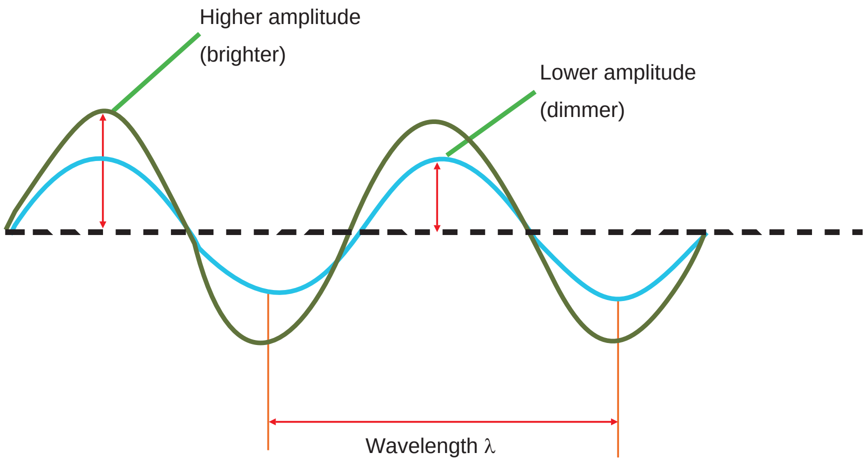


Figure 2.5 Amplitude (intensity) of waves.

Light of a particular shade of red, for instance, always has the same frequency and wavelength, but it can be dim (*low amplitude*) or bright (*high amplitude*).

Visible light occupies a small portion of the continuum of radiant energy which is known as the electromagnetic spectrum (Figure 2.6). The electromagnetic waves in the different spectral region travel at the same speed but differ in frequency and wavelength.

The long wavelength, low-frequency portion of the spectrum comprises the microwave and radiowave regions. The infrared (IR) region overlaps the microwave region on one end and the visible region on the other.

We perceive different wave lengths (*or frequencies*) of visible light as different colours, from red (λ = 750 nm) to violet (λ = 400 nm). Light of a single wavelength is called monochromatic (*Greek "one colour"*), whereas light of many wavelengths is polychromatic (*Greek "many colours"*). White light is polychromatic.

The region adjacent to visible light on the short-wavelength end consists of ultraviolet (UV) radiation. Still shorter wavelengths (*higher frequencies*) make up the X-ray and gamma ray (γ-ray) regions.

Thus, a TV signal, Infrared (IR) light, and a gamma ray emitted by a radioactive element differ principally in frequency and wavelength.

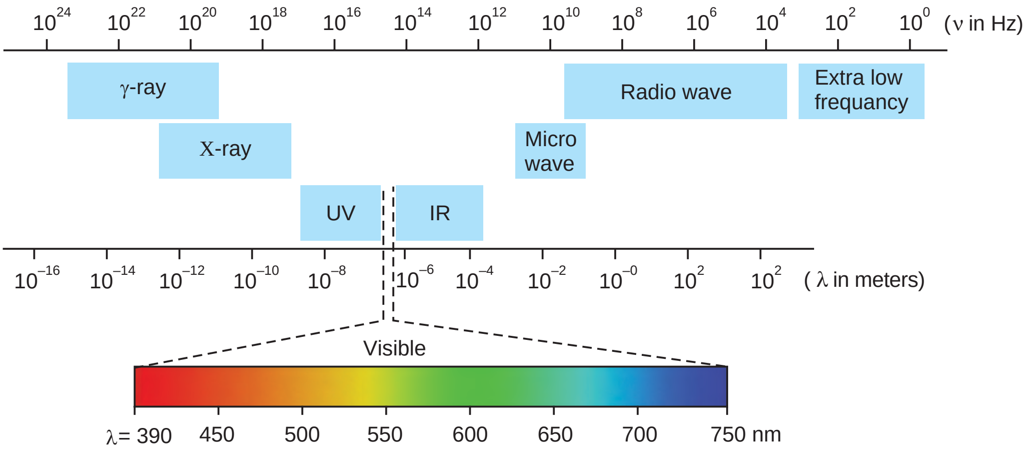


Figure 2.6 Regions of the electromagnetic spectrum.

Example 2.3

1. The yellow light given off by a sodium lamp has a wavelength of 589 nm. What is the frequency of this radiation?
2. A dental hygienist uses X-ray (λ = 1.00 Å) to take a series of dental radiographs while the patient listens to an FM radio station (λ = 325 cm) and looks out the window at the blue sky (λ = 473 nm). What is the frequency (in s^{-1}) of the electromagnetic radiation for each source?

Solution:

1. Rearranging Equation 2.1, and $\nu = c_o/\lambda$.

   We insert the value for c and ? and then convert nm to m. This gives us

$$\nu = \frac{3.00\times10^8 \text{m/s}}{589 \text{ nm}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1}$$

2. Because we are provided with the wavelengths, we can find the frequencies from Equation 2.1. Since c_o has units of m s^{-1}, we first convert the entire wavelength to metres.

For X-ray,

$$\lambda = 1.00 \cancel{\text{Å}} \times \frac{10^{-10} \text{m}}{1 \cancel{\text{Å}}} = 1.00\times10^{-10} \text{ m}$$

$$\lambda = c_o/\lambda = \frac{3.00\times10^8 \text{m/s}}{1.00\times10^{-10} \text{m}} = 3.00\times10^{18} \text{ s}^{-1}$$

For the radio station, $\lambda = 325 \text{ cm} \times \frac{1 \text{ m}}{100 \text{ cm}} = 3.25 \text{ m}$

$$\nu = \frac{3.00\times10^8 \text{m/s}}{3.25 \text{m}} = 9.23 \times 10^7 \text{ s}^{-1}$$

For the blue sky, $\lambda = 473 \text{ nm} \times \frac{10^{-9} \text{m}}{1 \text{ nm}} = 4.37 \times 10^{-7} \text{ m}$

$$\nu = \frac{3.00\times10^8 \text{ m/s}}{4.73\times10^{-7} \text{m}} = 6.34 \times 10^{14} \text{ s}^{-1}$$

Exercise 2.3

1. Some diamonds appear yellow because they contain nitrogeneous compounds that absorb purple light of frequency $7.23\times10^{14}\ s^{-1}$. Calculate the wavelength (in nm) of the absorbed light.
2. The FM station broadcasts traditional music at 102 MHz on your radio. Units for FM frequencies are given in megahertz (MHz). Find the wavelength of these radio waves in meters (m), nanometers (nm), and angstrom (Å).

2.5.2 The Quantum Theory and Photon

Soon after Rutherford had proposed his nuclear model, a major problem arose with it. A nucleus and an electron attract each other, so if they are to remain apart, the energy of the electron's movement must balance the energy of attraction. However, the laws of physics had previously established that a charged particle moving in a curved path must give off energy. If this requirement is applied to an orbiting electron, why did not the electron continuously lose energy and spiral into the nucleus? Clearly, if electrons behaved the way as predicted in classical physics, all atoms would have collapsed a long time ago!

The breakthrough that soon followed forced a complete rethinking of the classical picture of matter and energy. In the macroscopic world, the two are distinct: matter occurs in pieces you can hold and weigh; you can change the amount of matter in a sample piece by piece. Energy is "*massless*"; its amount can be changed in a continuous manner. Matter moves in specific paths, whereas light travels in diffuse waves. As soon as 20th century scientists explored the subatomic world, however, these clear distinctions between particulate matter and wavelike energy began to fade. In the following sections, you will examine the theories and experiments that led to the view of a quantized or particulate nature of light.

The quantum theory is concerned with the rules that govern the gain or loss of energy from an object. In 1900, the German physicist Max Planck came to an entirely new view of matter and energy. He proposed that a hot glowing object could emit (or absorb) only certain amounts of energy.

$$E = nh\nu$$

where E is the energy of the radiation, ν is the frequency, n is a positive integer (n = 1, 2, 3, ...) called quantum number and h is proportionality constant now called Planck's constant. With energy in joules (J) and frequency in second (s^{-1}), h has units of J s; ($h = 6.626 \times 10^{-34}$ J s)

Planck's contribution was to perceive that when we deal with the gain or loss of energy from objects in the atomic size or subatomic-size range, the rules "seem" to be different from those that apply when we are dealing with the energy gain or loss from objects of ordinary dimensions.

A Very Crude Analogy Might Best Illustrate What is Involved

Imagine a large truck loaded with about 2 tons of fine-grained sand. Let us assume that the amount of sand on the truck is measured by a supersensitive scale that can measure the weight of the 2-ton object to the nearest gram. With this scale as our measuring device, the gain or loss of a few grains of sand from the truck would be too small to be measured. A spade-ful of sand might be added or removed with no change in the scale reading.

Now imagine a tiny little truck operated by a driver of the size of tiny ant. For this little truck, a full load of sand would consist of, perhaps, a dozen grains of sand of the same size as those carried by the large truck. In this microscopic world, the load on the truck can be added to or decreased only by rolling on or off one or more grains of sand. On the scale that weighs this tiny truck, even one grain of sand represents a substantial fraction of the load and is easily measurable.

In the given analogy, the sand represents energy. An object of ordinary or macroscopic dimensions, like the large truck, contains energy in so many tiny pieces that the gain or loss of individual pieces is completely unnoticed. On the other hand, an object of atomic dimensions, such as our imaginary little truck, contains such a small amount of energy that the gain or loss of even the smallest possible piece makes a substantial difference.

The essence of Planck's quantum theory is that there is such a thing as a smallest-allowable gain or loss of energy. Even though the amount of energy gained or lost at one time may be very tiny, there is a limit to how small it may be. Planck termed the smallest allowed increment of energy gained or lost a quantum of energy. In the analogy, a single grain of sand represents a quantum of sand "energy".

It should be kept in mind that rules regarding the gain or loss of energy are always the same, whether we are concerned with objects on the size scale of our ordinary experience or with microscopic objects. However, it is only when dealing with matter at the atomic level of size that the impact of the quantum restriction is evident. Humans, being creatures of macroscopic dimensions, had no reason to suppose that the quantum restriction existed until they devised means of observing the behaviour of matter at the atomic level. The major tool for doing this at the time of Planck's work was the observation of the radiant energy absorbed or emitted by matter.

An object can gain or lose energy by absorbing or emitting radiant energy. Planck assumed that the amount of energy gained or lost at the atomic level by the absorption or emission of radiation had to be a whole-number multiple of a constant, times the frequency of the radiant energy.

$$\Delta E = h\nu,\ 2h\nu,\ 3h\nu, \qquad \text{...(2.3)}$$

where ΔE is the amount of energy gained or lost. The smallest increment of energy at a given frequency, $h\nu$ is the quantum of energy.

Example 2.4

Calculate the amount of energy (*that is, the quantum of energy*) that an object can absorb from yellow light, whose wavelength is 589 nm.

Solution:

We obtain the magnitude of a quantum of energy absorbed from equation 2.3 ($\Delta E = h\nu$; $h = 6.626 \times 10^{-34}$ J s). The frequency, ν, is calculated from the given wavelength, $\nu = c_o/\lambda = 5.09 \times 10^{14}\ \text{s}^{-1}$. Thus, we have:

$$\Delta E = h\nu = 6.626 \times 10^{-34}\ \text{J s} \times 5.09 \times 1014\ \text{s}^{-1}$$

$$= 3.37 \times 10^{-19}\ \text{J}$$

At this stage, you may be wondering about the practical applications of Planck's quantum theory. Planck's theory has within it the seeds of a revolution for the way the physical world is perceived.

The Photoelectric Effect

Light shining on a clean metallic surface can cause the surface to emit electrons. This phenomenon is known as the photoelectric effect. For each metal, there is a minimum frequency of light (*threshold frequency*) below which no electrons are emitted, regardless of how intense the beam of light. In 1905, Albert Einstein (1879–1955) used the quantum theory to explain the photoelectric effect. He assumed that the radiant energy striking the metal surface is a stream of tiny energy packets. Each energy packet, called a photon, is a quantum of energy, $h\nu$.

$$E_{ph} = h\nu \qquad \text{...(2.4)}$$

where E_{ph} is the energy of a photon. Thus, radiant energy itself is considered to be quantized. Photons of high-frequency radiation have high energies, whereas photons of lower frequency radiation have lower energy.

When a photon is absorbed by the metal, its energy is transferred to an electron in the metal. A certain amount of energy is required for the electron to overcome the attractive forces that hold it within the metal. Otherwise, it cannot escape from the metal surface, even if the light beam is quite intense.

If a photon has sufficient energy, then an electron is emitted. If a photon has more than the minimum energy required to free an electron, the excess energy appears as the kinetic energy of the emitted electron. This situation is summarized by the equation

$$h\nu = E_k + E_b \qquad \text{...(2.5)}$$

where E_k is the kinetic energy of the ejected electron, and E_b is the binding energy of the electron in the metal. Rewriting equation (2.5), using

$$E_k = ½\, m_e v^2 \text{ and } E_b = h\nu_o$$

results in

$$h\nu = h\nu_o + ½\, m_e v^2$$

where m_e is mass of an electron, and ν_o is the threshold frequency. Equation (2.5) shows that the more energetic the photon (*high frequency*), the higher the velocity of the ejected electron.

Now consider two beams of light having the same frequency (*which is greater than the threshold frequency*) but different intensities. The more intense beam of light consists of a larger number of photons. Consequently, it ejects more electrons from the metal's surface than the weaker beam of light. Thus, the more intense the light the greater the number of electrons emitted by the target metal. The higher the frequency of the light, the greater will be the kinetic energy of the emitted electrons.

Fortunately, we have equations to quantify these observations on the nature of the photoelectric effect. Fore example,

$$\Delta E = h\nu = h\nu_o + ½\, m_e v^2 \qquad \text{...(2.6)}$$

where ν_o is the threshold frequency, m_e is the mass of the electron and v is the velocity of the emitted electron. The energy (ΔE) of a quantum of radiation ($h\nu$) that goes into ejecting a photoelectron out of the metal (*the work function* $h\nu_o$) and the binding energy gives us the kinetic energy (½ mv^2). Equation 2.6 is one example of the first law of thermodynamics.

To understand the photoelectric effect, consider the analogy of a truck stuck in the mud. A stream of people can come by, and each of them individually can give a push without getting the truck unstuck. A small tractor also would have less than the threshold energy necessary to dislodge the truck. A farm tractor on the other hand, would be able to overcome the attractive forces of the mud and get the truck out. Larger tractors also could do the job. Some could even exert more pull than necessary thus giving the freed truck some kinetic energy.

Example 2.5

The maximum kinetic energy of the photoelectrons emitted from a metal is 1.03×10^{-19} J when light that has a 656 nm wavelength shines on the surface. Determine the threshold frequency, v_o, for this metal. Given quantities: $h = 6.626 \times 10^{-34}$ J s, $\lambda = 656$ nm, kinetic energy of photoelectron $E_k = 1.03 \times 10^{-19}$ J.

Solution:

Solve for v from $c_o = v \times \lambda$

$$v = c_o/\lambda \quad \frac{3.00\times10^{+8}\,\mathrm{m/s}}{656\mathrm{nm}\times10^{-9}\,\mathrm{m/mn}} = 4.57 \times 10^{14}\ \mathrm{s}^{-1}$$

Rearrange Equation 2.1 and solve for ν_o

$$\nu_o = \frac{h\nu - E_k}{h}$$

$$= \frac{(6.626\times10^{-34}\ \mathrm{J\,s}\times4.57\times10^{14}\ \mathrm{s}^{-1}) - (1.03\times10^{-19}\ \mathrm{J})}{6.626\times10^{-34}\ \mathrm{J\,s}} = 3.02 \times 1014\ \mathrm{s}^{-1}$$

Therefore, a frequency of 3.02×10^{14} Hz is the minimum (threshold) required to evoke the photoelectric effect for this metal.

Note! The wavelength λ_o corresponding to ν_o is given by $\lambda_o = c/\nu_o$. For this example,

$$\lambda_o = \frac{3.00 \times 10^8 \text{ m/s}}{3.02 \times 10^{-14} \text{ s}^{-1}} = 9.93 \times 10^{-7} \text{ m or } 993 \text{ nm.}$$

Photoelectrons will not be emitted from the surface of this metal unless the wavelength of the light is shorter than 993 nm. Remember that higher energies are associated with higher frequencies and shorter wavelengths.

Exercise 2.4

1. List the similarities between microwaves and ultraviolet radiation.
2. How does intensity of a radiation affect the kinetic energy of photons during photoelectric effect?

3. The threshold frequency for metallic potassium is 5.46×10^{14} s^{-1}. Calculate the maximum kinetic energy and velocity that the emitted electron has when the wavelength of light shining on the potassium surface is 350 nm. (The mass of an electron is 9.11×10^{-31} kg.)
4. A laser produces red light of wavelength 632.8 nm. Calculate the energy, in kJ, of one mole of photons of this red light.
5. Two members of the boron family owe their names to bright lines in their emission spectra. Indium has a bright indigo-blue line (451.1 nm), and thallium has a bright green line (535.0 nm). What are the energies of these two spectral lines?

2.5.3 Atomic Spectra

Atomic or line spectra are produced from the emission of photons of electromagnetic radiation (light).

When an element is vaporized, and thermally or electrically excited, it emits light with discrete frequencies. If dispersed by a prism, the light does not create a continuous spectrum, or rainbow, as sunlight does. Rather, it produces a line spectrum, a series of fine lines of individual colours separated by colourless (*black*) spaces.

The wavelengths at which the coloured lines occur are characteristic of the element (Figure 2.7). A line spectrum that consists of only relatively few wavelengths that is produced from light emitted by excited atoms is the unique feature of an element, and can be used for identification purposes.

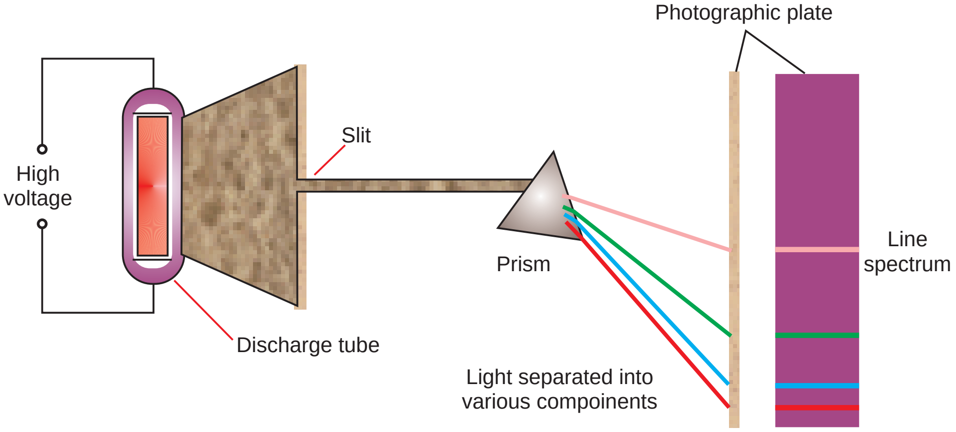


Figure 2.7 An experimental arrangement for studying the emission spectra of atoms and molecules.

2.5.4 The Bohr Model of the Hydrogen Atom

In 1913, Niels Bohr, a Danish physicist, who had worked with Rutherford, combined ideas from classical physics and the new quantum theory to explain the structure of the hydrogen atom. He suggested a model for the hydrogen atom that predicted the existence of line spectra. In doing so, he was able to explain the spectrum of radiation emitted by hydrogen atoms in gas-discharge tubes.

Based on the work of Planck and Einstein, Bohr made the revolutionary assumption that certain properties of the electron in a hydrogen atom – including energy, can have only certain specific values. That is to say, these properties are quantized. Bohr proposed the following three postulates for his model.

1. The hydrogen atom has only certain allowable energy levels, called stationary states. Each of these states is associated with a fixed circular orbit of the electron around the nucleus.
2. The atom does not radiate energy while in one of its stationary states. That is, even though it violates the ideas of classical physics, the atom does not change energy while the electron moves within an orbit.

3. The electron moves to another stationary state (*orbit*) only by absorbing or emitting a photon whose energy equals the difference in the energy between the two states.

$$E_{ph} = E_f - E_i = h\nu \qquad \text{...(2.7)}$$

The subscripts f and i represent the final and the initial states, respectively. The Bohr radius, denoted by a_o (a_o = 0.0529 nm) can be calculated using the formula

$$a_{\text{o}} = \frac{r}{n^2} \qquad \text{...(2.8)}$$

where n is a positive integer which is called quantum number.

r is the radius of the orbit and is given by:

$$r = \frac{n^2 \varepsilon_{\circ} h^2}{\pi m_e e^2 z} \qquad \text{...(2.9)}$$

where ε_{o} is the vacuum dielectric constant ($\varepsilon_{\text{o}} = 8.854 \times 10^{-12}\ \text{C V}^{-1}\ \text{m}^{-1}$).

A spectral line results from the emission of a photon of specific energy (*and therefore, of specific frequency*), when the electron moves from a higher energy state to a lower one. An atomic spectrum appears as lines rather than as a continuum because the atom's energy has only certain discrete energy levels or states.

In Bohr's model, the quantum number n (n = 1, 2, 3, ...) is associated with the radius of the electron's orbit, which is directly related to the atom's energy. The lower the quantum number, the smaller is the radius of the orbit and the lower is the energy level of the atom. When the electron is in the orbit closest to the nucleus (n = 1), the atom is in its lowest (first) energy level, which is called the ground state. By absorbing a photon whose energy equals the difference between the first and second energy levels, the electron can move to the next orbit. This second energy level (second stationary state) and all higher levels are called excited states. The hydrogen atom in the second energy level (first excited state) can return to the ground state by emitting a photon of a particular frequency:

$$\Delta E = E_e - E_g \qquad \text{...(2.10)}$$

where E_g and E_e represent the ground and the excited energy states, respectively.

When a sample of atomic hydrogen absorbs energy, different hydrogen atoms absorb different amounts. Even though each atom has only one electron, so many atoms are present that all the allowable energy levels (orbits) are populated by electrons. When an electron drops from orbits with $n > 3$ (*second excited state*), the infrared series of spectral lines is produced *i.e*, Paschen Series. The visible series arises from the photons emitted when an electron drops to the $n = 2$ orbit *i.e*, Balmer Series (*first excited state*), and the ultraviolet series arises when these higher energy electrons drop to the $n = 1$ orbit (*ground state*).

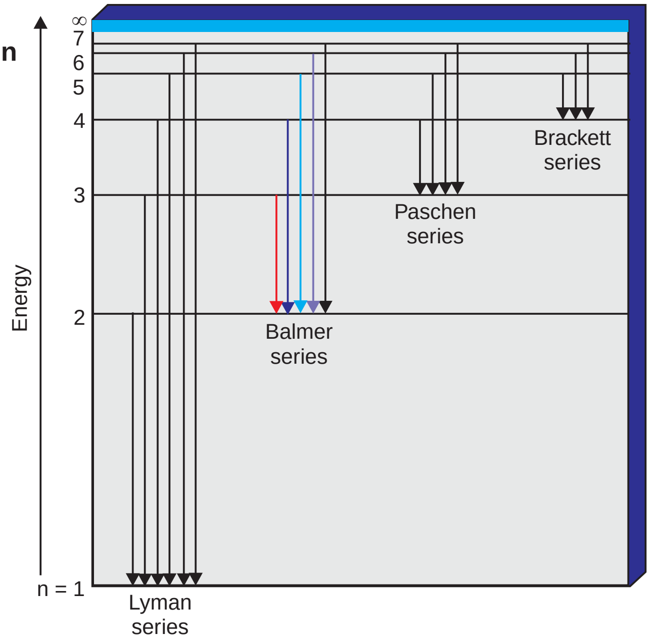


Figure 2.8 Representation of the observed spectral lines of the hydrogen atom.

Since a larger orbit radius means a higher atomic energy level, the farther the electron drops, the greater is the energy (higher v, shorter λ) of the emitted photon. The spectral lines of hydrogen become closer and closer together in the short wavelength (*high energy*) region of each series because the difference in energy associated with the jump from initial state (n_i) to the final state (n_f) becomes smaller and smaller as the distance from the nucleus increases.

Having made this basic assumption, Bohr was then able to use classical physics to calculate properties of the hydrogen atom. In particular, he derived an equation for the electron energy (E_n). Each specified energy value (E_1, E_2, E_3,...) is called an energy level of the atom. A very useful result from Bohr's work is an equation for calculating the energy levels of an atom,

$$E_n = -A \times \frac{Z^2}{n^2} \qquad \text{...(2.11)}$$

where A is the constant, has a value of, $A = 2.18 \times 10^{-18}$ J. The number n is an integer called the principal quantum number (n = 1, 2, 3, ...). Z is the charge of the nucleus. The negative sign in the equation appears because it is defined as zero energy when the electron is completely moved form the nucleus, i.e. $E_n = 0$ when $n = \infty$, so, $E_n < 0$ for any smaller n.

A can be expressed in terms of Rydberg constant as $A = hCR_H$, where R_H is Rydberg constant with a value of $1.0967 \times 10^7 M^{-1}$

For the H atom, Z = 1, so we have

$$E_n = -2.18 \times 10^{-18}\ \text{J} \times \frac{1}{n^2} \qquad \text{...(2.12)}$$

Therefore, the energy of the ground state n = 1 is -2.18×10^{-18} J. This equation is easily adapted to find the energy difference between any two levels:

$$\Delta E = hv = E_f - E_i = -2.18 \times 10^{-18}\ \text{J} \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad \text{...(2.13)}$$

Exercise 2.5

1. The H atom and the Be^{3+} ion each have one electron. Does the Bohr model predict their spectra accurately? Would you expect their line spectra to be identical? Explain.
2. Calculate the energies of the states of the hydrogen atom with n = 2 and n = 3, and calculate the wavelength of the photon emitted by the atom when an electron makes a transition between these two states.
3. What is the wavelength of a photon emitted during a transition from the n_i = 5 state to the n_f = 2 state in the hydrogen atom?
4. How much energy, in kilojoules per mole, is released when an electron makes a transition from n = 5 to n = 2 in an hydrogen atom? Is this energy sufficient to break the H–H bond (436 kJ / mol is needed to break this bond)?

5. Five lines in the H atom spectrum have wavelengths (in Å):

a	1212.7	b	4340.5	c	4861.3
d	6562.8	e	10938d		

Three lines result from transition to $n_f = 2$ (*visible series*). The other two result from transitions in different series-one with $n_f = 1$, and the other with $n_f = 3$. Identify n_i for each line.

2.5.5 Limitations of the Bohr Theory

The Bohr model of an atom was successful in accounting for the spectral lines of H-atom which indicated that he was on the right track. Despite its great success in accounting for the spectral lines of the H atom, the Bohr model failed to predict the wavelengths of spectral lines of atoms more complicated than hydrogen, even that of helium, the next simplest element. It works beautifully for the hydrogen atom and for other one-electron species such as He^+ and Li^{2+}. Bohr could not explain the further splitting of spectral lines in the hydrogen spectra on application of magnetic field and electric fields.

In the years following Bohr's development of a model for the hydrogen atom, the dual nature of radiant energy had become a familiar concept. Depending on the experimental circumstances, radiation might appear to have either a wave-like or particle-like (*photon*) character.

Is it possible that under proper circumstances, matter can behave as waves?

Louis de Broglie made a rather bold intuitive extension of this idea. Using Einstein's equation and Planck's equation for energy, he proposed that a particle with a mass, m, moving at a speed, v, has a wave nature consistent with a wavelength given by:

$$\lambda = \frac{h}{mv} \qquad \text{...(2.14)}$$

where h is Planck's constant. The quantity mv for any object is called its momentum. The matter waves describe the wave characteristics of material particles.

Because de Broglie's hypothesis is perfectly general, any object of mass m and velocity v would give rise to a characteristic matter wave. However, it is easy to see from Equation 2.14 that the wavelength associated with an object of ordinary size, such as a tennis ball is so tiny as to be completely out of the range of any possible observation. This is not so for electrons, because their mass is very small.

If de Broglie's concept is correct and all particles travel in waves, electrons should exhibit the typical wave-properties, diffraction and interference.

Electron particles with mass and charge create diffraction patterns, just as electromagnetic waves do. Although electrons do not have orbits of fixed radius, de Broglie thought that the energy levels of the atom are related to the wave nature of the electron.

The unsettling truth is that matter as well as energy show both behaviours: each possesses both "*properties*". In some experiments, one property is observed, while in other experiments, the other property is observed. The distinction between a particle and a wave is only meaningful in the macroscopic world - it disappears at the atomic level. The distinction is in the minds and the limiting definitions of people, not in nature. This dual character of matter and energy is known as the wave-particle duality.

Example 2.6

1. Calculate the de Broglie wavelength of an electron that has a velocity of 1.00×10^6 m/s. (electron mass, $m_e = 9.11 \times 10^{-31}$ kg; $h = 6.626 \times 10^{-34}$ J s)
2. Calculate the frequency of the hydrogen line that corresponds to the transition of the electron from the $n = 4$ to the $n = 2$ state.

Solution:

1. $$\lambda = \frac{h}{m_e v} = \frac{6.626\times10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{(9.11\times10^{-31}\text{kg})(1.00\times10^{6}\text{m s}^{-1})}$$

$$= 7.27 \times 10^{-10}\ \text{m}$$

2. We employ equation 2.13, $$\Delta E = -R_H \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = h\nu$$

$$\nu = -\frac{R_H}{h} \times \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Substituting $n_i = 4$ and $n_f = 2$:

$$\nu = -\left(\frac{2.179\times10^{-18}\,\text{J}}{6.626\times10^{-34}\ \text{J s}}\right)\left(\frac{1}{4^2} - \frac{1}{2^2}\right)$$

$$\nu = -\left(\frac{2.179\times10^{-18}\,\text{J}}{6.626\times10^{-34}\,\text{J s}}\right)\times\left(-\frac{3}{16}\right) = 6.17 \times 10^{14}\ \text{s}^{-1}$$

Exercise 2.6

1. What is the characteristic wavelength of an electron (in nm) that has a velocity of 5.97×10^6 m s^{-1} ($m_e = 9.11 \times 10^{-31}$ kg)?
2. Calculate the energy required for the ionization of an electron from the ground state of the hydrogen atom.
3. Calculate the wavelength (in nm) of a photon emitted when a hydrogen atom undergoes a transition from $n = 5$ to $n = 2$.

2.6 THE QUANTUM MECHANICAL MODEL OF THE ATOM

At the end of this section, you should be able to:

- state the Heisenberg uncertainty principle
- describe the significance of electron probability distribution;
- explain the quantum numbers n, l, m_l and m_s;
- write all possible sets of quantum numbers of electrons in an atom; and
- describe the shape of orbitals that are designated by *s*, *p*, and *d*.

Activity 2.13

Make a group and discuss the following:

If particles have wavelike motion, why don't we observe that motion in the macroscopic world?

If electron possess particle nature it should be possible to locate electron. How can an electron be located?

Is there any wave associated with a moving elephant? Share your ideas with the rest of the class.

Bohr's model was very important because it introduced the idea of quantized energy states for electrons in atoms. This feature is incorporated in our current model of the atom, the quantum mechanical model of the atom.

The sophisticated mathematical description of atomic structure based on the wave properties of subatomic particles is called wave mechanics or quantum mechanics. Principally, the Austrian physicist Erwin Scrödinger developed a model of the hydrogen atom based on the wave nature of the electron in the late 1920s. Mathematical equations describing the nature of electron waves in atoms are fundamental to the modern picture of the atom. The wave equations that are acceptable solutions to the Schrödinger equation are called wave functions. To obtain one of these acceptable solutions, we must assign integral values called quantum numbers to three quantities in the wave equation. This requirement is similar to the requirement for an integral value of n in the Bohr equation for the hydrogen atom.

In contrast to the precise planetary orbits of the Bohr atom, the wave mechanics picture of the hydrogen atom is less certain. Instead of determining the exact location of the electron, we can only speak of the probability of the electron being found in certain regions of the atom. Or, if we adopt the view that the electron is just a cloud of negative electric charge, we can only speak of the charge densities in various parts of the atom.

2.6.1 The Heisenberg's Principle

Discovery of the wave properties of matter raised a new and very interesting question. If a subatomic particle can exhibit the properties of a wave, is it possible to say precisely where that particle is located? One can hardly speak of the precise location of a wave. A wave, as a whole, extends in space. Its location is therefore not defined precisely. To describe the limitation (problem) of trying to locate a subatomic particle that behaves like a wave, Heisenberg formulated what is known as the Heisenberg uncertainty principle, which states that it is impossible to know simultaneously both the momentum p ($p = mv$) and the position of a particle with certainty. Mathematically, the Heisenberg's uncertainty principle is given as

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

where Δx and Δp are the uncertainties in measuring the position and momentum, respectively.

The above equation says that if we measure the momentum of a particle precisely (*i.e.* if Δp is made very small), then the position will be correspondingly less precise (*i.e*, Δx will become larger). Similarly, if the position of a particle is known more precisely, then its momentum will be less precise.

The German physicist Werner Heisenberg in 1927 concluded that there is a fundamental limitation to know both the location and the momentum of a particle simultaneously, which is due to dual behaviour of matter and radiation. Just as in the case of quantum effects, the limitation becomes important only when we deal with matter at the subatomic level, that is, with mass as small as that of an electron.

2.6.2 Quantum Numbers

An atomic orbital is specified first by three quantum numbers that are associated respectively, with the orbital's size (*energy*), shape, orientation and, later, independent of these three quantum numbers, the electron spin. The first three sets of quantum numbers have a hierarchical relationship: the size-related number limits the shape-related number, the shape-related number in turn limits the orientation-related number.

Three among the four quantum numbers characterize the orbitals in the atom. That is, they describe the orbital or the space the electron is supposed to occupy. The fourth quantum number is used to describe the spin of the electrons that occupy the orbitals.

The four quantum numbers are:

1. The principal quantum number (n) is a positive integer having values $n = 1, 2, 3, \ldots$. It gives the following information:

   (*i*) Relative size of the orbital or the relative distance of the electron from the nucleus. Size of orbital increases with the increase of principal quantum number n.

   (*ii*) Energy of the orbital. Higher the n value, greater is the energy. For example: when the electron occupies an orbital with $n = 1$, the hydrogen atom is in its ground state and has lower energy than when the electron occupies an orbital with $n = 2$ (*first excited state*).

   (*iii*) Maximum number of electrons present in any shell (given by the formula $2n^2$).

2. The azimuthal quantum number (l) is also known as angular momentum or subsidiary quantum number. It is an integer having values from 0 to ($n - 1$). For an orbital with $n = 1$, l can have a value only of 0. For orbitals with $n = 2$, l can have a value of 0 or 1; for those with $n = 3$, l can be 0, 1 or 2; etc. So, the number of possible l values equals the value of n. *For a given value of n, the maximum possible value of l is ($n - 1$).* The azimuthal quantum number gives the following information:

(*i*) Number of subshell present within any shell.

(*ii*) It describes the shape of the orbital and is sometimes also called the orbital-shape quantum number.

3. The magnetic quantum number (m_l) is also known as the orbital-orientation quantum number. It is an integer having values from $-l$ through 0 to $+l$. The possible values of an orbital's magnetic quantum number are set by its angular momentum quantum number (*that is, l determines m_l*). An orbital with $l = 0$ can have only $m_l = 0$. However an orbital with $l = 1$, can have m_l value of –1, 0, or + 1; thus there are three possible orbitals with $l = 1$ each with its own spatial orientation. *The number of possible m_l values or orbitals for a given l value is $(2l + 1)$. It prescribes the orientation* of the orbital in the three-dimensional space about the nucleus.

4. The electron spin quantum number (m_s) has only two possible values, +½ (*represented by the arrow,* ↑) and – ½ (represented by the arrow ↓). The name electron spin quantum suggests that electrons have a spinning motion. However, there is no way to attach a precise physical reality to electron spin.

   The quantum numbers specify the energy states of the atom.

   - The atom's energy levels or shells are given by the n value.
   - The atom's sublevels or subshells are given by the n and l values. Each level contains sublevels that designate the shape of the orbital.
   - The atom's orbitals are specified by the n, l and m_l values. Thus, the three quantum numbers that describe an orbital express its size (energy), shape and spatial orientation. Each sublevel is designated by a letter:

l = 0, is an *s* sublevel

l = 1, is a *p* sublevel

l = 2, is a *d* sublevel

l = 3, is a *f* sublevel

The letters *s*, *p*, *d*, and *f* are derived from the names of spectroscopic lines: *s*, sharp; *p*, principal; *d*, diffuse; and *f*, fundamental. Sublevels are named by joining the n value and the letter designation. For example, the sublevel (subshell) with $n = 2$, $l = 0$ is called the 2*s* sublevel; the only orbital in this sublevel has $n = 2$, $l = 0$ and $m_l = 0$. A sublevel with $n = 3$, $l = 1$, is a 3*p* sublevel. It has three possible orbitals: one with $n = 3$, $l = 1$ and $m_l = -1$; another with $n = 3$, $l = 1$ and $m_l = 0$ and the third $n = 3$, $l = 1$, and $m_l = +1$.

For a given principal quantum number, *n*, the total number of orbitals is determined as:

Number of orbitals = n^2 in a shell.

Similarly, the number of orbitals in each subshell is determined as:

Number of orbitals in a subshell = $2l+1$.

Example 2.7

1. What values of the angular momentum quantum number (l) and magnetic quantum number (m_l) are allowed for a principal quantum number (n) of 3? How many orbitals are allowed for $n = 3$?
2. Give the name, magnetic quantum numbers, and numbers of orbitals for each sublevel with the following quantum numbers:

a $n = 3$, $l = 2$

b $n = 2$, $l = 0$

c $n = 5$, $l = 1$

d $n = 4$, $l = 3$

3. What is wrong with each of the following quantum number designations and/or sublevel names?

	n	l	m_l	Name
a	1	2	0	1*p*
b	4	3	+1	4*d*
c	3	1	-2	3*p*

Solution:

1. Determining *l* values:

For $n = 3$, $l = 0, 1, 2$

Determining m_l for each *l* value:

For $l = 0$, $m_l = 0$

For $l = 1$, $m_l = -1, 0, +1$

For $l = 2$, $m_l = -2, -1, 0, +1, +2$

Number of orbitals = n^2, n is 3 and $n^2 = 3^2 = 9$ orbitals

3s : 1 orbital

3p : 3 orbitals

3d : 5 ortbitlas

Total = 9 orbitals

2.

	n	l	sublevel name	Possible m_l values	number of orbitals
a	3	2	3*d*	−2, −1, 0, +1, +2	5
b	2	0	2*s*	0	1
c	5	1	5*p*	−1, 0, +1	3
d	4	3	4*f*	−3,−2, −1, 0, +1, +2, +3	7

3. a A sublevel of $n = 1$ can have only $l = 0$, not $l = 1$. The only possible sub shell is 1*s*.

   b A sublevel with $l = 3$ is an *f* sublevel, not a *d* sublevel. The sublevel name should be 4*f*.

   c A sublevel with $l = 1$can have only m_l of -1, 0, +1, not -2.

Exercise 2.7

1. Give the sublevel notation for each of the following sets of quantum numbers.
   - a $n = 3$, $l = 2$
   - b $n = 2$, $l = 0$
   - c $n = 4$, $l = 1$
   - d $n = 4$, $l = 3$
2. Indicate whether each of the following is a permissible set of quantum numbers. If the set is not permissible, state why it is not.
   - a $n = 3$, $l = 1$, $m_l = +2$
   - b $n = 4$, $l = 3$, $m_l = -3$
   - c $n = 3$, $l = 2$, $m_l = -2$
   - d $n = 0$, $l = 0$, $m_l = 0$
   - e $n = 3$, $l = 3$, $m_l = -3$
3. Consider the electronic configuration of an atom:
   - a What are the n, l and m_l quantum numbers corresponding to the 3*s* orbital?

b List all the possible quantum number values for an orbital in the 5*f* sub shell.

c In which specific subshell will an electron be present if the quantum numbers $n = 3$, $l = 1$, and $m_l = -1$?

4. Which of the quantum numbers relates to the electron only? Which relate (*s*) to the orbital?

2.6.3 Shapes of Atomic Orbitals

The wave mechanical picture of an electron in an *s*-orbital looks like a ball made of a raised soft hairy rug (*that is the orbital has spherical symmetry*).

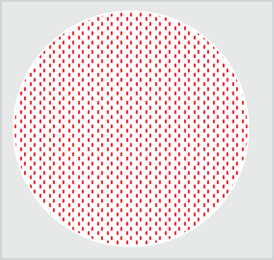


Figure 2.9 a Geometric shape of 1*s*-orbital.

The 2*s*-orbital also has spherical symmetry.

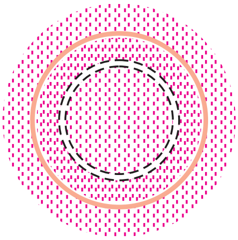


Figure 2.9 b Geometric shape of 2*s*-orbital.

Higher level *s*-orbitals (3*s*, 4*s*, ...) have similar overall shapes, that is, spherical symmetry. The second principal energy level ($n = 2$) consists of four different orbitals. One having $l = 0$, is the 2*s* orbital just described. The other three orbitals of the $n = 2$ level have $l = 1$. They are described by dumb bell-shaped regions (Figure 2.10).

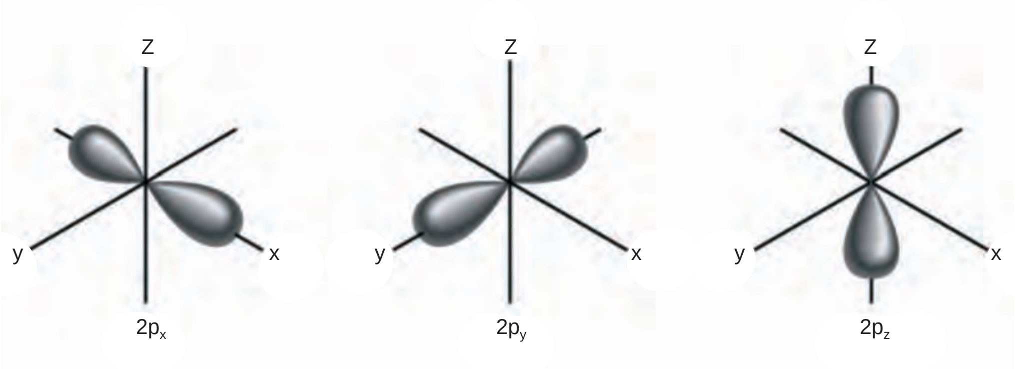


Figure 2.10 The three *p* -orbitals.

Two lobes lie along a line with the nucleus at the centre between the lobes. The different 2*p* orbitals are referred to as the $2p_x$, $2p_y$ and $2p_z$, orbitals, because they are perpendicular to one another and can be drawn along the *x*, *y*, and *z* coordinate axes (see Figure 2.10). Higher - level *p*-orbitals (that is 3*p*, 4*p*, ...) have similar overall shapes.

The third principal energy level (*n* = 3) is divided in to three sublevels: one 3*s* orbital, three 3*p* orbitals, and five 3*d* orbitals. The *d* orbitals are described in Figure 2.11.They are much more complex in shape than *p* orbitals.

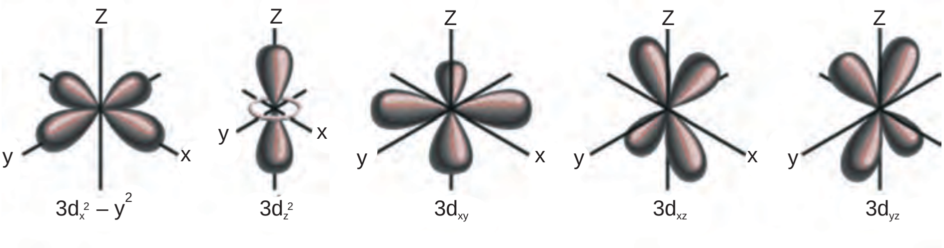


Figure 2.11 The five *d* orbitals.

The fourth principal energy level is divided in to four sublevels or subshells. There are one 4s subshell with one orbital, a 4*p* subshell with three orbitals, a 4*d* subshell with five orbitals, and a 4*f* subshell with seven orbitals. The *f* orbitals have complex shapes.

2.7 ELECTRONIC CONFIGURATIONS AND ORBITAL DIAGRAMS

At the end of this section, you should be able to:

- explain the Aufbau principle;
- explain the Pauli exclusion principle;
- explain Hund's rule; and
- write ground-state electronic configurations of multi-electron atoms.

Activity 2.14

Form a group and discuss the given questions. After discussion share your ideas with rest of the class.

1. Why are there never more than two electrons in an atomic orbital?
2. When there are two electrons in an orbital, why do these always have opposing spins?
3. Why are orbitals occupied singly first before the pairing of electrons occurs?
4. Why do the electrons in singly-occupied orbitals have parallel spins?

Several questions arise when you look carefully at the electron configuration of an atom. To answer these questions, it is necessary to know the basic principles that govern the distribution of electrons among atomic orbitals. The electron configuration for any atom follows the following three principles:

Aufbau Principle. In general, electrons occupy the lowest-energy orbital available before entering the higher energy orbital.

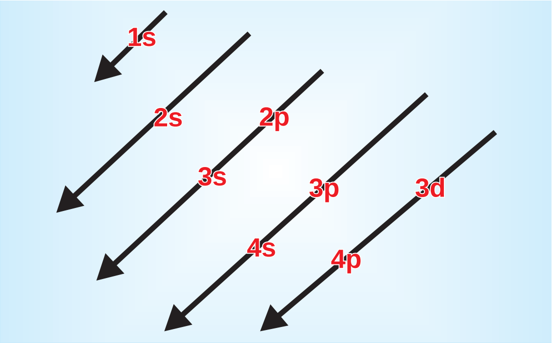


Figure: 2.12 Increasing order of filling orbitals.

Hund's Principle. Equal energy orbitals (degenerate orbitals) are each occupied by a single electron before the second electrons of opposite spin enters the orbital. In other words, each of the three 2*p* orbitals ($2p_x$, $2p_y$ and $2p_z$) will hold a single electron before any of them receives a second electron.

Pauli's Exclusion Principle. No two electrons can have the same four quantum numbers. *i.e.* they must differ in at least one of the four quantum numbers.

***Note:** aufbau is a German word, which means building-up, while Pauli and Hund are the names of scientists.*

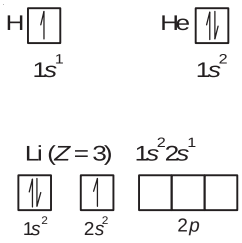
2.7.1 Ground State Electronic Configuration of the Elements

The electronic configuration of an atom describes the distribution of the electrons among atomic orbitals in the atom. Two general methods are used to denote electron configurations. The subshell (sublevel) notation uses numbers to designate the principal energy levels or principal quantum number and the letters *s*, *p*, *d* and *f* to identify the sublevels or subshells. A superscript number following a letter indicates the number of electrons in the designated subshell (*e*). The designation can be written as nl^e. The electron configurations for hydrogen (H; Z = 1), helium (He; Z = 2) and lithium (Li; Z = 3) are $1s^1$, $1s^2$, $1s^2\ 2s^1$ respectively.

Activity 2.15

Form a group and discuss the reason why the notation nl^e does not include electron spin quantum numbers.

The other way to present this information is through an orbital diagram, which consists of a box (*or circle, or just a line*) for each orbital available in a given energy level, grouped by sublevel, with an arrow indicating the electron's presence and its direction of spin. Traditionally ↑, $m_s = +½$ and ↓, $m_s = –½$, but these are arbitrary, so it is necessary only to be consistent. The orbital diagrams for the first three elements are:

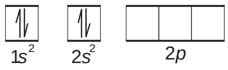


In Li, the 2*s* orbital is only half-filled, so the fourth electron of beryllium fills in with its spin paired: $n = 2$, $l = 0$, $m_l = 0$, $m_s = +½$.

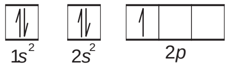
For beryllium, the 2*s* sublevel is filled, and the next lower energy sublevel is the 2*p*. The three orbitals in the 2*p* sublevel have equal energy (same *n* and *l* values), which means that the fifth electron of boron can go into any one of the 2*p* orbitals. Since a *p* sublevel has $l = 1$, the m_l (orientation) values can be –1, 0, or +1. For convenience, the boxes are lebelled from left to right, –1, 0, +1, and assume it enters the m_l = –1 orbital: n = 2, l = 1, m_l = –1, and m_s = +½.

For our purposes here, the designation of m_l = –1 for this boron electron (*and the box we chose to label* –1, *in which we placed the arrow*) is arbitrary. The 2p orbital's have equal energy and differ only in their orientation.

Be $(Z = 4) 1s^2 2s^2$



B $(Z = 5) 1s^2 2s^2 2p^1$



Activity 2.16

Form a group and discuss the following question:

1. What does each box in an orbital diagram represent?
2. Which quantity is represented by the direction (either up or down) of the half arrows in an orbital diagram?
3. Is Hund's rule used in deriving the electron configuration of beryllium?

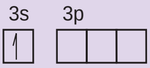
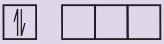
Share your ideas with the rest of the class.

Exercise 2.8

1. Write the ground-state electron configuration for potassium
2. Write the electron configuration of an element with atomic number 10.
3. Write the electron configuration of an element with (Z = 20 and A = 40 m_u).
4. Draw the orbital diagrams for the valence electrons of the atoms: C, N, O, F and Ne and determine the number of unpaired electrons for each atom.

Activity 2.17

Form a group and complete the electron configuration for the period 3 elements of perodic table.

Atomic Number	Element	Orbital diagram	Full electron configuration	Condensed electron configuration
11	Na		[$1s^2\ 2s^2\ 2p^6\ 3s^1$]	[Ne] $3s^1$
12	Mg		[$1s^2\ 2s^2\ 2p^6\ 3s^2$]	[Ne] $3s^2$
13	Al			
14	Si			
15	P			
16	S			
17	Cl			
18	Ar			

Group Assignment

Form a group and discuss on the following questions. Share your ideas with the rest of the class.

Select any ten elements. For each of your chosen elements, prepare an index card. In the upper left-hand corner of the card, place a box like the one on the periodic table, name, and the atomic mass of the element.

Do some research on the element and write a few sentences about its properties and uses. Attach either an object or a picture to the card that shows its properties. For example for carbon, you could attach a pencil lead. For mercury, you might have a picture of a thermometer. Make a large periodic table, using your cards. Show the result to your classmates.

Table 2.2 Maximum capacities of subshells and principal shells

n	1	2	3	4
l	0	0, 1	0, 1, 2	0, 1, 2, 3
Subshell designation	*s*	*s*, *p*	*s*, *p*, *d*	*s*, *p*, *d*, *f*
Orbital in subshell	1	1, 3	1, 3, 5	1, 3, 5, 7
Subshell capacity	2	2, 6	2, 6, 10	2, 6, 10, 14
Principal shell capacity	2	8	18	32

Activity 2.18

Form a group and complete the following table for the first row transition metals on your note book

Atomic Number	Element	Orbital Diagram	Electron configuration (ground state)	Condensed Electron configuration
21	Sc			
22	Ti			
23	V			
24	Cr			
25	Mn			
26	Fe			
27	Co			
28	Ni			
29	Cu			

Examine the electron configurations of chromium and copper. The expected configuration, those based on the aufbau principle, is not the ones observed through the emission spectra and magnetic properties of the elements.

	Expected	**Observed**
Cr (Z = 24)	[Ar] $4s^2 3d^4$	[Ar] $4s^1 3d^5$
Cu (Z = 29)	[Ar] $4s^2 3d^9$	[Ar] $4s^1 3d^{10}$

The reason for these exceptions to the aufbau principle are not completely understood, but it seems that the half-filled 3*d* subshell of chromium ($3d^5$) and the fully filled 3d subshell of copper ($3d^{10}$) lends a special stability to the electron configurations. Apparently, having a half-filled 4s subshell and a half-filled 3*d* subshell gives a lower energy state for a Cr atom than having a filled 4s subshell.

Because there is little difference between the 4*s* and 3*d* orbital energies, expected and observed electron configurations are quite close in energy.

At higher principal quantum numbers, the energy difference between certain subshell is even smaller than that between the 3*d* and 4*s* subshells. As a result, there are still more exceptions to the Aufabu principle among the heavier transition elements.

Exercise 2.9

1. Write the electron configuration for the Co^{3+}, Cl^{-} , Al^{+}, Cr, As^{-}, and Cu.
2. Write the electron configuration and the orbital diagram of the first excited state of sodium. (Hint: The outermost electron is excited).
3. What is the electron capacity of the n^{th} energy level? What is the capacity of the fourth energy level?

2.8 ELECTRONIC CONFIGURATIONS AND THE PERIODIC TABLE OF THE ELEMENTS

At the end of this section, you should be able to:

- correlate the electron configuration of elements with the periodicity of elements;
- give a reasonable explanation for shape of the periodic table;
- classify elements as representative, transition and inner-transition elements;
- explain the general trends in atomic radius, ionization energy, electron affinity, electronegativity; and metallic character of elements within a period and group of the periodic table; and
- write the advantages of the periodic classification of elements.

2.8.1 The Modern Periodic Table

Activity 2.19

Form a group and assign codes to the first twenty elements in the periodic table by the letters from *a* to *t*.

The following are some of the properties of the coded elements:

1. *b*, *g*, *j*, *o*, *p*, *s* and *t* are the only metals.
2. *p* and *o* form amphoteric hydroxides.

3. *b*, *j*, *s* and *t* show characteristics colour of the flame test for their chlorides.
4. *a* and *r* can form covalent hydrides of empirical formula XH_2, the hydroxides of *l* is a mild reducing agent, while that of *e* is not.
5. *i*, *c* and *q* do not form oxides, hydrides or chlorides; their boiling points are −260°C, −246°C and −186°C respectively.
6. The dissociation energy of molecular a is smaller than that of *r*.
7. *f* and *k* form oxides of empirical formula X_2O_5. On hydrolysis, the oxide of *f* yields a much more acidic solution than that of *k*.
8. *n* forms an oxide which has high melting point and is an important raw material of glass.

Identify the codeed elements and place them in the correct positions in the periodic table, and giving reasons for doing so.

9. Discuss on the drawbacks of Mendeleev's periodic table and the need for the modern one.

You have studied in Grade 9 that the modern periodic table of the elements is one of the great classifying schemes in science and has become an indispensable tool to chemists.

Periodic relationships can be summarized by the general statement called periodic law. In its modern form, the periodic law states that certain sets of physical and chemical properties recur at regular intervals (periodically) when the elements are arranged according to increasing atomic number.

Activity 2.20

Form a group and discuss the following questions:

1. Do the elements having last electron in s orbital form a family?
2. Is there some variations in physical and chemical properties of these elements?
3. Why are some elements placed out of the main body of periodic table?
4. Where are isotopes located?
5. Can the properties of a compound formed be predicted on the basis of the location of its combining elements in the periodic table?

2.8.2 Classification of the Elements

Activity 2.21

Form a group and discuss the following questions:

1. How can the 90 or so naturally occurring elements be classified?
2. Are they all separate and distinct?
3. Is there a need to learn about 90 different elements as well as some thousands of their compounds?
4. What could be the basis of classifying elements?

Elements are placed in the periodic table in accordance to valence electron entering the orbital of lowest energy. There are 18 groups and 7 periods in the modern periodic table.

Representative or main group elements: These consist of all *s*- and *p*-block elements. The chemical properties of the representative elements are determined by the number of valence electrons in their atoms.

Transition elements: These are *d*-block elements. There are four series of transitional elements, 3*d*, 4*d*, 5*d* and 6*d* depending on the energy levels of *d*-orbitals.

Inner transition elements: These are the *f*-block elements. There are two series of *f*-block elements, 4*f* and 5*f* series called lanthanides and actinides, respectively. The periodic table is unable to include the inner transition elements in its main frame. They have been allotted the same single place in the periodic table though their electronic configurations are not identical. Besides, the variation in their properties is not much.

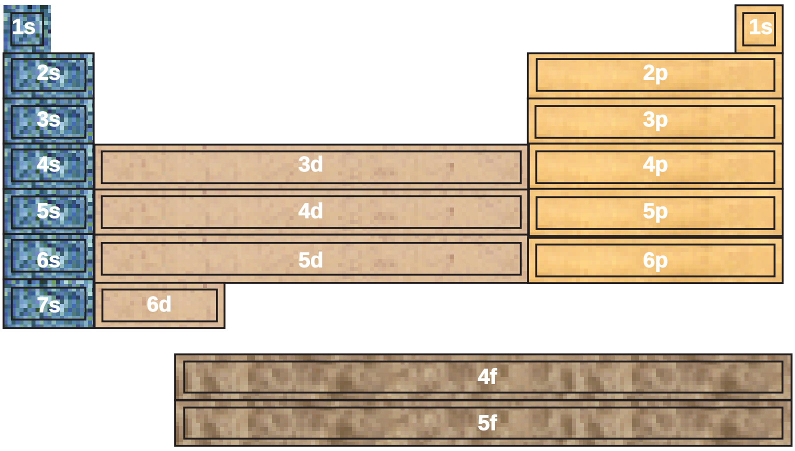


Figure 2.13 Classification of elements according to the type of subshells being filled.

2.8.3 Periodic Properties

Activity 2.22

Form a group and discuss the following questions:

1. How does size of elements vary across a period?
2. Why are elements of Group1 and 2 called metals, while those of Group 17 non-metals?
3. Why elements of Group18 are least reactive?
4. Define shielding effect and effective nuclear charge.

Some physical properties, such as thermal and electrical conductivity, density, and hardness are displayed only by bulk matter, that is, by large aggregations of atoms. In this section you will examine some periodic atomic properties like atomic radii, ionization energies, electron affinities, electronegativity, and metallic character.

Atomic Size (Atomic Radii)

Activity 2.23

Form a group and discuss on the following questions:

1. Why the sizes of atoms do not increase uniformly with increasing atomic number?
2. Why the difference in atomic radius between the elements $Z = 11$ (Na; 186 pm) and $Z = 12$ (Mg; 160 pm) is so large, where as between $Z = 24$ (Cr; 125pm) and $Z = 25$ (Mn; 124 pm) the difference is negligible.
3. In which location in the periodic table would you expect to find the elements having the largest atoms? Explain.
4. Why isoelentronic ions do not have the same ionic radii?
5. Why does the quantum-mechanical description of multi-electron atoms make it difficult to define the term atomic radius?
6. How do the sizes of atoms change as we move:
   a from left to right in a row in the periodic table?
   b from top to bottom in a group in the periodic table? Explain.
7. a Why does the He atom have a smaller radius than the H atom?
   b Why is the He atom smaller than the Ne atom? Explain.

Share your ideas with the rest of the class.

Exact size of an isolated atom cannot be measured because its outermost electrons have a chance of being found at relatively large distances from the nucleus. What can be measured is the distance between the nuclei of two adjacent atoms, and can derive a property called the atomic radius from this distance.

One of the most common methods to determine atomic radius is to assume that atoms are spheres that touch each other when they are bonded together (Figure 2.14).

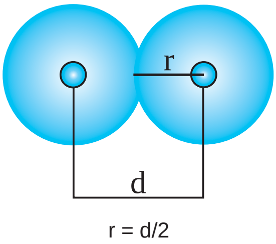


Figure 2.14 Atomic radius for a diatomic molecule.

Figure 2.14 depicts a way to define the radius of an atom using the distance *d* between the nuclei of two atoms on an element in a molecule. It is assumed that the atom is a hard sphere with a radius equal to half the bond distance, 1/2*d*.

For example, the distance between iodine atoms in an iodine molecule I_2, (I—I) is 2.66 Å, so we can define the radius of an iodine atom to be half this distance: 1.33 Å: similarly, the distance between iron atoms (Fe) in iron metal is 2.48Å. Therefore, each iron atom in the metal has a radius of 1.24Å.

Within a vertical group of the periodic table, each succeeding member has one more principal shell occupied by electrons, thus, atomic radii increases from top to bottom within a group of the periodic table. To describe how atomic radii vary within a period of the periodic table, it is helpful to employ a new concept. The effective nuclear charge (Z_{eff}) acting on an electron is the actual nuclear charge less the screening effect of other electrons in the atom.

For example, consider a sodium atom. If the 3*s* valence electron were at all times completely outside the region in which the ten electrons of the neon core ($1s^2\ 2s^2\ 2p^6$) are found, the 3*s* electron would be perfectly screened or shielded from the positively charged nucleus; it would experience an attraction to a net positive charge of only +11 – 10 = +1. The corresponding situation for magnesium atom would be that of the two 3s electrons outside the neon core and a net positive charge of +12 – 10 = +2 acting on each of the 3*s* electrons. Similarly it is found that the net positive charge acting on the valence electrons would progressively increase across the third period.

The effective nuclear charge increases from left to right in a period of representative elements in the periodic table. Because the effective nuclear charge increases, valence electrons are pulled in toward the nucleus and held more tightly. Atomic radii of the A-group elements (*main group element*) tend to decrease from left to right in a period of the periodic table.

The restriction to A-group elements is an important one. In a series of B-group elements (*transition elements*), electrons enter an inner electron shell, not the valence shell. In this process, the effective nuclear charge remains essentially constant instead of increasing. For example, compare the effective nuclear charges, Z_{eff}, of iron, cobalt, and nickel.

Fe: [Ar] $3d^6 4s^2$	Co: [Ar] $3d^7 4s^2$	Ni: [Ar] $3d^8\ 4s^2$
$Z_{eff} = +26 - 24 = +2$	$Z_{eff} = +27 - 25 = +2$	$Z_{eff} = +28 - 26 = +2$

Because the effective nuclear charges are almost the same, we conclude that the radii should also be almost the same. The actual values are 124, 124, and 125 pm, respectively, for Fe, Co and Ni.

Exercise 2.10

1. Arrange the following atoms in order of increasing atomic radius: F, P, S, As.
2. The atoms and ions Na, Mg^+, Al^{2+} and Si^{3+} all have the same number of electrons. For which of these will the effective nuclear charge acting on the outer most electron be the smallest? For which will it be greatest? Explain

Ionization Energy (IE)

Activity 2.24

Form a group and discuss on the following:

1. The trend in successive ionization energies as electrons are removed one at a time from an aluminum atom. Why is there a big jump between IE_3 and IE_4?
2. Why does sulphur have a lower first ionization energy than phosphorus?
3. The second ionization energy of lithium is much greater than that of beryllium. Explain.
4. For strontium, which quantity will be greater, the difference between IE_1 and IE_2 or the difference between IE_2 and IE_3?

Share your ideas with the rest of the class.

The ionization energy (IE) is the amount of energy required to remove the outermost electron in an isolated gaseous atom or ion.

Multi-electron atoms can lose more than one electron, so the ionization energies required to remove each electron are numbered in sequence from the ground-state atom. Consider for example the boron atom, which has five electrons, two in an inner core ($1s^2$) and three valence electrons ($2s^2 2p^1$). The five ionization steps and their ionization energies, IE_1 through IE_5, are:

$$\mathrm{B\,(g)} \rightarrow \mathrm{B^+\,(g)} + e^-; \qquad \mathrm{IE_1} = 801\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{B^+\,(g)} \rightarrow \mathrm{B^{2+}\,(g)} + e^-; \qquad \mathrm{IE_2} = 2427\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{B^{2+}\,(g)} \rightarrow \mathrm{B^{3+}\,(g)} + e^-; \qquad \mathrm{IE_3} = 3660\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{B^{3+}\,(g)} \rightarrow \mathrm{B^{4+}\,(g)} + e^-; \qquad \mathrm{IE_4} = 25{,}025\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{B^{4+}\,(g)} \rightarrow \mathrm{B^{5+}\,(g)} + e^-; \qquad \mathrm{IE_5} = 32{,}822\ \mathrm{kJ\ mol^{-1}}$$

The first ionization eneergy (IE_1) is the energy needed to remove an electron from the highest occupied sublevel of the gaseous atom.

$$\mathrm{Atom(g)} \rightarrow \mathrm{Ion^+(g)} + \mathrm{e^-} \qquad \Delta \mathrm{E} = \mathrm{IE_1} > 0$$

The second ionization energy (IE_2) removes the second electron. Since the electron is being pulled away from a positively charged ion, IE_2 is always larger than IE_1:

$$\mathrm{Ion^+\,(g)} \rightarrow \mathrm{Ion^{2+}\,(g)} + \mathrm{e^-} \qquad \Delta E = \mathrm{IE_2} \quad (\text{always} > \mathrm{IE_1})$$

The first ionization energy is a key factor in an elements chemical reactivity because, atoms with a low IE_1 tend to form cations during reactions, whereas those with a high IE_1, (*except the noble gases*) often form anions.

The elements exhibit a periodic change in first ionization energy. There is a roughly inverse relationship between IE_1 and atomic size.

The only significant deviations from this pattern occur in Group IIIA. Although IE_1 decreases as expected from boron (B) to aluminium (Al), no decrease occurs for the rest of the group. As with the atomic size trends, filling the d sublevels of the intervening transition elements in period 4, 5 and 6 causes a greater than expected Z_{eff}, which holds the outer electrons tightly in this larger IIIA members.

As we move across a period, Z_{eff} generally increases so atomic radii become smaller. As a result, the attraction between the nucleus and the outer electrons increases, so an electron becomes more difficult to remove. In general, ionization energy increases across a period; it is easier to remove an electron from an alkali metal than from a noble gas.

There are two exceptions in the otherwise smooth increase in ionization energy trend, which occur at Groups IIIA and VIA in period 2 (at B and at O) and in period 3 (at Al and at S). The first deviation occurs because the np sublevel is higher in energy than the ns sublevel. The second deviation occurs because the np^4 *electron occupies the same orbital as another np electron, the first such pairing, so electron repulsions raise the orbital energy. Removing this electron relieves the repulsions and leaves a stable, half-filled np sublevel; thus the fourth p electron is pulled off more easily.*

For the representative elements, removing a core electron requires much more energy compared to removing a valence electron.

Group Assignment

Form a group and discuss on the following questions. Share your ideas with the rest of the class.

Plot the first ionization energy of the first 18 elements against atomic number. On the same graph, make a plot of the second ionization energy of the first 18 elements. Consult chemistry books for the required information.

Is second IE less than first IE for an element?

Compare the second IE values of sodium and magnesium.

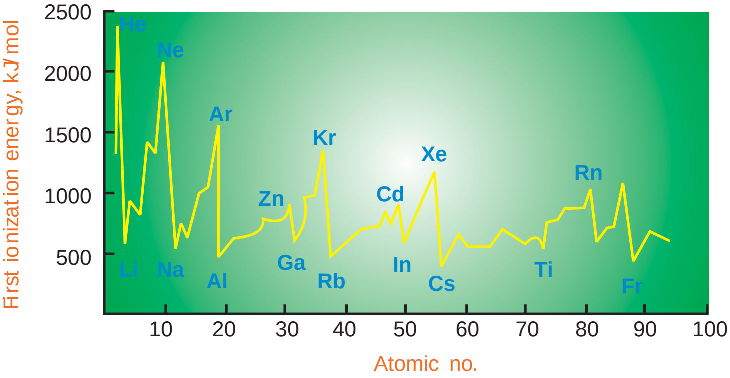


Figure 2.15 A graph of first ionization energy versus atomic number.

Example 2.8

Explain the irregularities in the trends across periods.

1. Boron, with $Z = 5$ and the electron configuration $1s^22s^22p^1$, has smaller first ionization energy (801 kJ mol^{-1}) than does beryllium ($Z = 4$), which has the electron configuration $1s^22s^2$ and IE_1 = 900 kJ mol^{-1}.

   Solution: The 2*p* electron of boron is at a higher energy than the 2*s* electron of beryllium and is therefore easier to remove. This kind of discontinuity occurs generally in proceeding from a Group IIA or Group IIB elements to a Group IIIA element.

2. IE_1 values for nitrogen ($[He]2s^22p_x^1\,p_y^1p_z^1$) is higher than oxygen ($[He]2s^22p_x^2p_y^1p_z^1$).

   Solution: The observed IE_1 values are 1314 kJ/mol for oxygen and 1402 kJ/mol for nitrogen. In 2*p* orbitals, the repulsion between the paired electrons in the $2p_x$ orbital of oxygen makes the removal of one of those electrons easier to accomplish than the removal of an unpaired electron from the half-occupied 2*p* orbital of nitrogen.

Table 2.3 Ionization energies of some selected elements (in kJ mol^{-1})

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
	Li	Be	B	C	N	O	F	Ne
IE_1	520	900	801	1086	1402	1314	1681	2081
IE_2	7298	1757						
	Na	Mg						
IE_1	496	738						
IE_2	4562	1451						
	K	Ca						
IE_1	419	590						
IE_2	3059	1145						
	Rb	Sr						
IE_1	403	550						
IE_2	2633	1064						

Exercise 2.11

1. Use the third period of the periodic table as an example to illustrate change in the first ionization energies of the elements as we move from left to right. Explain the trend.
2. Ionization energy measurements are usually carried out with atoms in the gaseous state. Why?
3. The first and second ionization energies of K are 419 kJ mol^{-1} and 3052 kJ mol^{-1} and those of Ca are 590 kJ mol^{-1} and 1145 kJ mol^{-1}, respectively, compare their value and comment on the differences.
4. Why does potassium have a lower first ionization than lithium?
5. Based on their positions in the periodic table, predict which atom of the following pairs will have larger first ionization energy:

   a Ga, Ge　　b Br, Sb　　c K, Cr,　　d Mg, Sr　　e O, Ne

Electron Affinity (EA)

Ionization energy refers to the process of forming a gaseous positive ion from a gaseous atom. The corresponding atomic property for the formation of a gaseous negative ion is electron affinity, the energy change that occurs when an electron is added to a gaseous atom or ion.

An electron approaching a neutral atom experiences an attraction for the positively charged nucleus. Repulsion of the incoming electron by electrons already present in the atom tends to offset this attraction. Still, in many cases the incoming electron is absorbed by the atom and energy is evolved as in the process:

$$F\,(g) + e^- \rightarrow F^-\,(g); \quad EA = -328 \text{ kJ mol}^{-1}$$

When a fluorine atom gains an electron, energy is given off. The process is exothermic and the electron affinity is therefore a negative quantity.

Activity 2.25

Form a group and discuss on the following:

1. By using electron configurations, explain why the electron affinity of F is negative value whereas the electron affinity of Ne is a positive value.
2. Which group of elements has electron affinities with the largest negative values? Explain why.
3. Silicon has an electron affinity of –134 kJ/mol. The electron affinity of phosphorus is –72 kJ/mol. Give a plausible reason for this difference.

Share your ideas with the rest of the class.

Table 2.4 Electron affinities of some selected elements (in kJ mol^{-1})

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Li	Be	B	C	N	O	F	Ne
–60	0	–27	–154	–7	–141	–328	–
Na	Mg	Al	Si	P	S	Cl	
–53	0	-44	–20	–200	–200	–349	
K	Ca	Ga	Ge	As	Se	Br	
–48	0	–36	–116	–195	–195	324	
Rs	Sr	In	Sn	Sb	Te	I	
–46	0	–34	–121	–190	–190	–295	
Cs				Bi	Po	At	
–47				–183	–270	–270	

Table 2.4 lists several electron affinity values but we observe fewer clear-cut trends and more irregularities than in the Table 2.3, listing the ionization energies of some elements. The given information suggest a rough correlation between electron affinity and atomic size. Smaller an atom, more negative is its electron affinity. The smaller the atom the closer an added electron can approach the atomic nucleus and the more strongly it is attracted to the nucleus. This certainly seems to be the case for the Group IA elements, for Group VIA from S to Po and for Group VIIA from Cl to At. The first row elements present some problems. The electron affinity of O is not as negative as that of S, nor is that of F as negative as that of Cl. Here it may be that electron repulsions in the small compact atoms keep the added electron from being tightly bound as we might expect.

In most cases, the added electron goes into an energy sublevel that is already partly filled. For the Group IIA and VIIIA atoms, however, the added electron would be required to enter a significantly higher energy level, the *np* level for the Group IIA atoms and the *s* level for the next principal level for the Group VIIIA atoms. In these cases a stable anion does not form.

As the stepwise loss of multiple electrons in the formation of positive ions has been described, in the same manner, the stepwise addition of electrons in anion formation can be described, and we can write a separate electron affinity for each step. For oxygen atom, it can be written as:

$$O(g) + e^- \rightarrow O^- (g); \quad EA_1 = -141 \text{ kJ mol}^{-1}$$

$$O^-(g) + 1e^- \rightarrow O^{2-}(g); \quad EA_2 = +744 \text{ kJ mol}^{-1}$$

Activity 2.26

Form a group and discuss the possible reasons why EA_2 is a positive quantity for oxygen atom.

Share your ideas with the rest of the class.

Electronegativity

Atoms of the elements in the upper right of the periodic table (small, non-metal atoms) attract bonding electrons most strongly. Therefore, they have the greatest electronegativities. Atoms of the elements to the left side of the table (large, metal atoms) have a weaker hold on electrons. They have the smallest electronegativities. On an electronegativity scale devised by Linus Pauling, the most non-metallic and hence most electronegative element, fluorine, is assigned a value of 4.0. Typical active metals have electronegativities of about 1.0 or less.

Within a period of the periodic table, elements become more electronegative from left to right. In the second period, the trend is regular.

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0

That is, it increases by about 0.5 per element as we move from lithium at the far left to fluorine at the far right. In other periods the trend is in the same direction but less regular;

Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0

Within a group, electronegativity decreases from top to bottom. Chlorine is less electronegative than fluorine and sulphur is less electronegative than oxygen. A comparison of electronegativities is not quite straight forward when considering two elements that are neither in the same period nor in the same group.

Activity 2.27

Form a group and discuss on the following:

1. What is the electronegativtiy of an atom? How is it different from electron affinity? Discuss in groups.
2. In a given family of the periodic table, what is the general relationship between electronegativity and size?

Share your ideas with the rest of the class.

Metallic Character

Activity 2.28

Form a group and summarize the trend in metallic character as a function of position in the periodic table. Is it the same as the trend observed for atomic size and Ionization energy?

Share your ideas with the rest of the class.

Metallic character refers to the chemical properties associated with elements classified as metals. These properties arise from the elements ability to lose electrons. As one moves across a period from left to right in the periodic table, the metallic character decreases, as atoms are more likely to gain electrons to fill their valance shell rather than to lose them to remove the shell. Down a group, the metallic character increases, due to the lesser attraction from the nucleus to the valence electrons.

2.8.4 Advantages of Periodic Classification of the Elements

Activity 2.29

Form a group and discuss the following:

a In which region of the periodic table do you locate metals?

b In which region are the elements with general electronic configuration of ns^2p^5 located? Give group number.

c Write group number and period of an element with atomic number 34.

d Is an element with the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^1$ a metal or a non- metal? Will it form a cation or an anion readily? Give appropriate reason.

e An element is located in Group 18 and 2nd Period of the modern periodic table. On the basis of this information predict the reactivity of the element.

f An element X of 3rd Period has very low IE_1 and largest size in the period. Specify possible group numbers.

Some of the advantages of periodic classification of elements are:

1. The classification of elements is based on the atomic number, which is a fundamental property of an element.
2. The reason for placing isotopes at one place is justified as the classification is on the basis of atomic number.
3. It explains the periodicity of the properties of the elements and relates them to their electronic configurations.
4. The position of the elements that were misfits on the basis of mass number (anomalous pairs like argon and potassium) could be justified on the basis of atomic number.
5. The lanthanides and actinides are placed separately at the bottom of the periodic table.
6. The table is simple, systematic and easy way for remembering the properties of various elements as it is based on the electronic configuration.

Unit Summary

- *Cathode rays (electrons) are produced when electricity passes through evacuated tubes. X-rays form when cathode rays strike matter.*
- *Radioactivity is the emission of radiation by unstable nuclei, and the most common types of radiations are alpha (α) particles, beta (β) particles and gamma (γ) rays. Alpha particles are helium nuclei; beta particles are electrons; and gamma rays are high frequency electromagnetic radiation similar to X-rays.*
- *Rutherford's atomic model is that of a very small positively charged nucleus and extra-nuclear electrons. The nucleus consists of protons and neutrons and contains practically all the mass of an atom. Atomic masses and relative abundances of the isotopes of an element can be established by mass spectrometry. The atomic mass of the element is the average of these mass numbers based on their percentage abundances.*

- *Electromagnetic radiation is the transmission of electric and magnetic fields as a wave motion. The waves are characterized by their velocity in a medium:* $c = \nu\lambda$. *A light source that emits an essentially unbroken series of wavelength components has a continuous spectrum. Only a discrete set of wavelength components is present in the emission spectrum of an atom.*
- *Einstein's explanation of the photoelectric effect views light as packets of energy called photons. The energy of the photon* (E_{ph}) *is given by the expression* $E = h\nu$ *where h is Planck's constant.*
- *Bohr's theory requires the electron in a hydrogen atom to be in one of a discrete set of energy levels. The fall of an electron from a higher to a lower energy level releases a discrete amount of energy as a photon of light with a characteristic frequency.*
- *Bohr's theory accounts for the observed atomic spectrum of hydrogen atom.*
- *The electron in a hydrogen atom can be viewed as a matter-wave enveloping the nucleus. The matter-wave is represented by a wave equation, and solutions of the wave equation are wave functions. Each wavefunction is characterized by the value of four quantum numbers: the principal quantum number, n; the angular momentum quantum number l; the magnetic quantum number, ml; and the spin quantum number, ms. Wave functions with acceptable values of the three are called atomic orbitals. An orbital describes a region in an atom that has a high probability of containing an electron or a high electron change density. Orbitals with the same value of n are in the same principal energy level or principal shell. Those with the same value of n and of l are in the same sublevel or subshell. The shapes associated with orbitals depend on the value of l. Thus, the s orbital* ($l = 0$) *is spherical and the p orbital* ($l = 1$) *is dumbbell-shaped.*
- *The n, l and* m_l *quantum numbers define an orbital, but a fourth quantum number is also required to characterize an electron in an orbital - the spin quantum number, ms. This quantum number may have either of two values: +½ or –½.*
- *The wave mechanical treatment of the hydrogen atom can be extended to multi-electron atoms, but with this essential difference: principal energy levels are (i) lower than those of the hydrogen atom and (ii) split, that is, having different energies for the different subshells.*

- *Electron configuration refers to the distribution of electrons among orbitals in an atom. Introduced here are the subshell notations (or "s,p,d, f") and the orbital diagram. Key ideas required to write a probable electron configuration are: (i) electrons tend to occupy the lowest energy orbitals available; (ii) no two electrons in an atom can have all four quantum numbers alike; and (iii) where ever possible, electrons occupy orbitals singly rather than in pairs.*
- *The Aufbau principle describes a hypothetical process of building up one atom from the atom of preceding atomic number. With this principle and the idea cited above, it is possible to predict probable electron configurations for many of the elements. In the Aufbau process, electrons are added to the s or p subshell of highest principal quantum number in the representative or main group elements. In transition elements, electrons go into the d subshell of the second last shell, and in the inner transition elements, into the f subshell of the third last shell.*
- *Elements with similar valence-shell electron configurations fall in the same group of the periodic table. For A-group elements, the group number corresponds to the number of electrons in the principal shell of highest quantum number. The period number is the same as the highest number of principal shell containing electrons (the outer shell). The division of the periodic table into s, p, d and f blocks greatly assists in the assignment of probable electron configurations.*
- *Certain atomic properties vary periodically, when atoms are considered in terms of increasing atomic number. The properties and trends considered in this unit are those of atomic radius, ionic radius, ionization energy and electron affinity. Values of these atomic properties strongly influence physical and chemical properties of the elements.*

Check List

Key terms of the unit

- *amplitude*
- *atomic mass*
- *atomic mass unit (amu)*
- *atomic number*
- *auf bau Principle*
- *cathode*
- *cathode rays*
- *charge/mass ratio*
- *Dalton's atomic theory*
- *effective nuclear charge*
- *electronic configuration*
- *electromagnetic radiation*
- *exited state*
- *ground state*

- *frequency*
- *Hund's Rule*
- *inner-transition metal*
- *isotope*
- *isotope atom*
- *mass number*
- *metalloid*
- *non-metal*
- *Pauli's Exclusion Principle*
- *period*
- *periodic law*
- *periodic table*
- *photon*
- *proton*
- *quantum numbers*
- *representative element*
- *s-block elements*
- *Schrödinger equation*
- *transition metal*
- *uncertainty principle*
- *wave length*

REVIEW EXERCISE

Part I: Multiple Choice Type Questions

1. The number of neutrons in an atom of $^{226}_{88}\text{Ra}$ is:

   a 88

   b 82

   c 138

   d 314

2. Which of the following are usually found in the nucleus of an atom?

   a Protons and neutrons only

   b Protons, neutrons and electrons

   c Neutrons only

   d Eelectrons and neutrons only

3. An atom has an atomic number of 31 and a mass numbers of 70. How many electrons will it have in its valence shell?

   a 5

   b 4

   c 3

   d 2

4. Which of the following would produce a line spectrum rather than a continuous spectrum?

   a Sunlight

   b Excited hydrogen atom

   c A normal filament light bulb

   d A yellow (*sodium*) street light

5. Among the following, which colour corresponds to light of the highest frequency?

   a Green
   b Red
   c Yellow
   d Blue

6. Which one of the following is not a valid electronic configuration?

   a 2, 8, 8, 2
   b 2, 8, 9, 1
   c 2, 6
   d 2, 8, 4

7. Which of the given elements will have the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$.

   a Neon atoms
   b Chlorine atoms
   c Magnesium ion
   d Calcium atoms

8. Which of the following elements has the lowest first ionization energy?

   a Potassium
   b Sodium
   c Calcium
   d Argon

9. How many 3*d* electrons are present in the ground state of chromium atom?

   a 9
   b 4
   c 6
   d 5

10. The first ionization energy of aluminium is slightly lower than that of magnesium because:

    a magnesium has a higher nuclear charge
    b the outer electron in aluminium is in a *p*-orbital not an *s*-orbital
    c in aluminium the electron is being lost from a doubly filled orbital
    d the radius of the aluminium atom is greater than that of the magnesium atom

11. Which of the following atoms would have the highest fourth ionization energy?

    a P
    b Si
    c N
    d C

12. How many unpaired electrons are there in the Cr^{3+} ion?

    a 6
    b 3
    c 1
    d 0

13. Which of the following species would require the highest energy for the removal of one electron?

a	Mg^{2+}	c	Ne
b	Na^{+}	d	F^{-}

14. Which of the following has the lowest electronegativity?

a	Carbon	c	Beryllium
b	Magnesium	d	Boron

15. Which of the following has the smallest radius?

a	Na	c	Mg
b	Na^{+}	d	Mg^{2+}

Part II: Answer the following questions:

16. Identify the following subatomic particles:
    - a The number of these in the nucleus is equal to the atomic number.
    - b The particle that is gained or lost when ions are formed.
    - c The particle that is not found in the nucleus.
    - d The particle that has no electrical charge.
    - e The particle that has a much lower mass than the others.

17. Calculate the number of protons, neutrons and electrons in the following:

Element	**Mass Number**	**Protons**	**Neutrons**	**Electrons**
Neon (Z = 10)	20			
Nitrogen (Z = 7)	14			
Gallium (Z = 31)	70			
Nickel (Z = 28)	59			
Iron (Z = 26)	56			

18. Carbon has atomic number 6. It comprises three isotopes, the first with 6 neutrons, the second with 7 neutrons, the third with 8 neutrons.
    - a Calculate the mass numbers of the three isotopes and represent them in the form of $^{x}_{y}C$
    - b Explain what is meant by "isotope"

c In naturally occurring copper isotopes, $^{63}_{29}\text{Cu}$ contributes 69.09% and $^{65}_{29}\text{Cu}$, 30.91%. Calculate the relative atomic mass of copper. (Accurate mass determined; $^{63}_{29}\text{Cu}$ = 62.9298 m_u, $^{65}_{29}\text{Cu}$ = 64.9278 m_u)

19. Two particles X and Y have the following composition:

    X: 17 protons, 18 neutrons, 17 electrons
    Y: 17protons, 18 neutrons, 18 electrons

    a What is the relationship between these particles?

    b Will these two particles have similar chemical properties? Explain why?

20. Arrange the following in order of increasing ionization energy: Li, Na, Ne, N, O

21. Explain the following:

    a The first ionization energy of beryllium is greater than that of boron.

    b The first ionization energy of oxygen is less than that of nitrogen.

    c The first ionization energy of lithium is greater than that of sodium.

22. The electron configuration of a particular metal cation M^{3+} is [Ar] $3d^2$.

    a Identify the corresponding metal.

    b Write the electron configuration of the metal atom.

23. Arrange the following in order of increasing atomic radius Mg, Cs, Ca, Al, Ba.

24. Explain briefly, why potassium always occurs as a +1 ion in its compounds and calcium as a +2 ion.

25. Arrange the atoms (ions) in each of the following groups in order of increasing size based on their location in the periodic table.

    a Mg^{2+}, O^{2-}, Na^{+}, F^{-}, Al^{3+}

    b Ne, N^{3-}, F^{-}, Na^{+}, C^{4-}

    c F, Be, C, B, Li

    d K^{+}, S^{2-}, As^{3-}, Cl^{-}, Ca^{2+}

26. Excited sodium atoms emit light with a wavelength of 589 nm. Calculate the:

    a frequency of the light, and

    b energy of one of these photons in joules

27. A hydrogen atom is excited to the $n = 8$ energy level. It emits a photon of light as it falls to the $n = 2$ energy level. Calculate the:

    a wavelength of light emitted, and

    b frequency of the light emitted

28. The electron of a hydrogen atom is in the $n = 3$ level. What is its energy?

29. Calculate the wavelength of the light emitted when an electron falls from $n = 3$ to the $n = 1$ state in hydrogen atom.

30. The photon emitted by a cyclotron has a velocity of 1.50×10^3 m s^{-1}. What is the wavelength of this photon? Given that the mass of photon = 1.676×10^{-27} kg and Planck's constant = 6.62×10^{-34} J.s.

31. Write the number and the letter for the orbital that corresponds to the following pairs of n and l quantum numbers:

    a $n = 3, l = 1$ c $n = 3, l = 2$

    b $n = 4, l = 0$ d $n = 5, l = 3$

32. Write the electron configurations for the following atoms and ions:

    a Fe^{3+} c Cr^{3+}

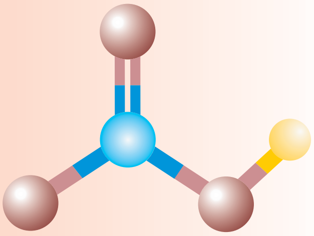
    b V d Al^{+}

33. Identify the transition element (*s*) from the following:

    a $_{40}Zr$ c $_{56}Fe$

    b $_{88}Ra$ d $_{36}Kr$

UNIT 3



Chemical Bonding and Structure

Unit Outcomes

At the end of this unit, you should be able to:

- *understand that a chemical bond is an attractive force between particles;*
- *demonstrate an understanding of the formation and general properties of substances containing ionic, covalent and metallic bonds;*
- *draw Lewis structures for simple ionic and covalent compounds;*
- *understand the origin of polarity within molecules;*
- *describe the formation and nature of hydrogen bonds, dipole-dipole forces and London forces;*
- *know the three different but related bonding models (Lewis model, Valence bond model and Molecular orbital model) and recognize the usefulness of the bonding theories in explaining and predicting molecular properties(bond angle, bond length, bond energy, etc;*
- *explain how the properties of a substance (solid or liquid) depends on the nature of the particles present and the type of intermolecular forces;*
- *appreciate the importance of intermolecular forces in plant and animal life;*

- *explain how the Valence Shell Electron Pair Repulsion (VSEPR) model can be used to predict molecular shape;*
- *Know the types of crystalline solid (ionic, molecular, covalent network, or metallic) formed by a substance and describe their properties;*
- *conduct experiments to observe and analyze the physical properties of different substances to determine the type of bonding present; and*
- *describe scientific enquiry skills along this unit: observing, inferring, predicting, classifying, comparing and contrasting, making models, communicating, asking questions, applying concepts, relating cause and effect and making generalizations.*

MAIN CONTENTS

3.1 INTRODUCTION

At the end of this section, you should be able to:

- describe the reason why atoms form chemical bonds;
- state octet rule;
- define chemical bonding; and
- describe the types of chemical bonding and their mechanisms of the bonding process.

Almost everything a person sees or touches in daily life, like the air we breathe, the food we eat, the clothes we wear, are the result of chemical bonds. The concept of chemical bonding lies at the very core of chemistry; it is what enables about little over one hundred elements to form millions of known chemical substances that make up our physical world.

In Grade 9, you have learned about chemical bonding and its types such as ionic, covalent and metallic bonding and their characteristics. In this unit, we will discuss some new concepts about chemical bonding, like molecular geometry, theories of chemical bonding and much more.

Activity 3.1

Form a group and discuss the following questions:

1. Why do atoms readily combine to form molecules?
2. Why molecules are more stable than free atoms?
3. What keeps the atoms together in a molecule?
4. Why do elements combine in certain fixed ratio?
5. The following diagram shows how energy varies as two H atoms approach each other to form H_2. Interpret the diagram to show the decrease in potential energy favouring bonding.

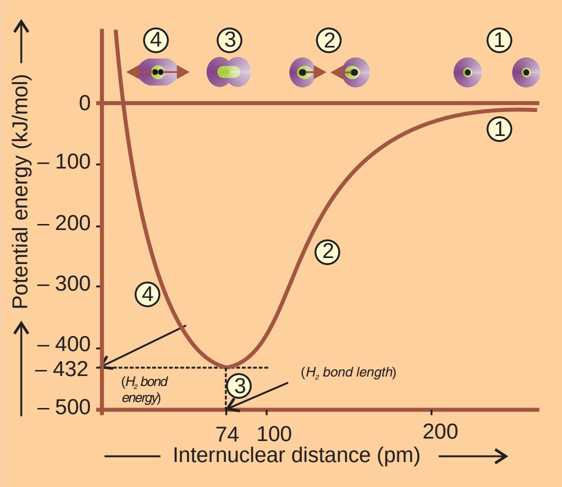


Figure 3.1 Energy diagram for hydrogen molecule.

3.1.1 Octet Rule

Activity 3.2

Form a group and discuss the following:

1. Why some atoms are very reluctant to combine with other atoms and exist as single atoms?
2. Is there any thing common amongst these atoms?
3. What is special about these atoms with respect to their electronic configuration?
4. What is the common name for this group of elements?
5. What is the reason for their stability?
6. Atoms lose or gain electrons not merly to satisfy the octet rule but to reach a lower energy state in an ionic compound. But it is in reaching this lower energy state that they often tend to follow the octet rule. Explain.

Share your ideas with the rest of the class.

You have studied in your earlier classes that noble gases have very stable electron arrangements such as 2; 2, 8; 2, 8, 8 and their outer shells are fully saturated. The first three are shown in Figure 3.2 and explains why noble gases are so reluctant to form compounds with other elements.

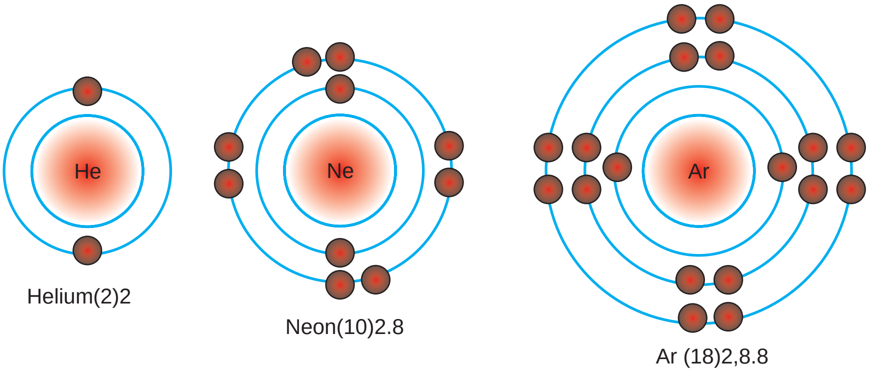


Figure 3.2 First three noble gases.

The noble gases have very stable electron configuration, as reflected by their high ionization energies, low electron affinity and general lack of reactivity. Because all noble gases (except He) have eight valence electrons, many atoms undergoing reaction also attain eight valence electrons. The ns^2np^6 electron configuration of the valence shell of all noble gas (except Helium) atoms, is commonly called an octet of electrons. The octet rule, a useful generalization that applies to all types of bonding which states that when atoms bond, they lose, gain or share electrons to attain the electronic configuration ns^2np^6 of the nearest noble gas. Nearly every main-group monoatomic ion has a filled outer level of electrons (*either two or eight*), the same number as in the nearest noble gas.

Compounds such as CH_4 and NH_3 obey octet rule, whereas others like $BeCl_2$, BF_3, SF_6 and PCl_5 though stable, but do not obey octet rule. Such compounds are exceptions to the octet rule. In such compounds the central atom is either short of electrons or has excess of electrons as compared to the octet. These are discussed later in this unit. Though there are certain exceptions to the octet rule, yet it provides us a useful framework for introducing many important concepts of bonding.

Note! Octet rule states that during the formation of a chemical compound, each atom has an octet (8) electrons in its highest occupied energy level by gaining, losing, or sharing electrons.

3.1.2 Types of Chemical Bonding

In Grade 9 you have learnt in details what exactly is a chemical bond? The forces of attraction that hold atoms together are called chemical bonds. Broadly these forces of attraction can be categorised as intramolecular forces, which affect the chemical properties of the species.

There are three main types of chemical bonds – covalent, ionic and metallic bonds. In general, there is a gradual change from more metallic to more non-metallic property when moving from left to right across a period and when moving from bottom to top within a group. Three types of bonding can result from the manner in which the atoms can combine:

Ionic Bonding is formed by electron transfer from a metal to a non-metal with different electronegativity values.

Covalent Bonding is formed as a result of electron sharing between two non-metals. If the electronegativity values are very similar then it is non-polar covalent bonding but if the electronegativity values are much different, then it is a polar covalent bonding.

Metallic Bonding refers to the interaction between the delocalised electrons and the metal nuclei.

Activity 3.3

Form a group and:

1. Illustrate the formation of ionic bond between the elements from Group IA, period 2 and Group VIIA and period 3. Correlate this bonding with the electronic configuration.
2. Indicate whether each of the following formulas is a likely formula for a stable ionic compound, and give explanation for your answer:

   a Rb_2O b $BaCl$ c MgF_3 d $ScBr_3$ e Na_3N

Share your ideas with the rest of the class.

3.2 IONIC BONDING

At the end of this section, you should be able to:

- define ionic bonding;
- use Lewis electron dot symbols to depict main group elements;

- describe ionic bonding using Lewis electron dot symbols;
- list the favourable conditions for the formation of ionic bond;
- explain the formation of ionic bonding;
- give examples of ionic compounds;
- define Lattice energy;
- calculate lattice energy of ionic crystal from a given data using the Born-Haber cycle;
- discuss the exceptions to octet rule;
- describe the properties of ionic bonding;
- carry an activity to demonstrate the effect of electricity on ionic compounds (PbI_2 and $NaCl$); and
- carry an activity to investigate the melting point and solubility of some ionic compounds ($NaCl$ and $CuCl_2$).

Activity 3.4

Form a group and discuss the following questions:

1. What types of elements are involved in ionic bonding?
2. What is ionization energy?
3. What role does electron affinity play in the formation of an ionic bond?
4. How many ionic bonds will result from the combination of magnesium and chlorine?
5. What type of bond will be formed between a metal and a non-metal?

Share your ideas with the rest of the class.

You are familiar with how sodium metal reacts with chlorine gas, Cl_2, to form sodium chloride, $NaCl$, a substance composed of Na^+ and Cl^- ions.

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

Let us look at the electronic configurations of sodium and chlorine atoms for a possible interpretation of the reaction between them. A sodium atom, Na, by losing an electron, forms a sodium ion, Na^+, which has the same electron configuration as the noble gas neon.

$$\begin{array}{lllll} \text{Na} & \rightarrow & \text{Na}^+ & + & e^- \\ [\text{Ne}]3s^1 & & [\text{Ne}] & & \end{array}$$

A chlorine atom, Cl, by gaining an electron, forms a chloride ion, Cl^-, which has the same electron configuration as the noble gas argon.

$$\begin{array}{lllll} \text{Cl} & + & e^- & \rightarrow & \text{Cl}^- \\ [\text{Ne}]3s^2\ 3p^5 & & & & [\text{Ar}] \end{array}$$

$$\begin{array}{llllll} \text{Na} & + & \text{Cl} & \rightarrow & \text{Na}^+ & + \quad \text{Cl}^- \\ [\text{Ne}]3s^1 & & [\text{Ne}]3s^2\ 3p^5 & & [\text{Ne}] & \quad\ [\text{Ar}] \end{array}$$

When particles have opposite electric charges, a force of attraction exists between them; known as electrostatic force of attraction. In sodium chloride, the sodium ions and the chloride ions are held together by electrostatic force of attraction, thus forming an ionic bond or electrovalent bond.

Exercise 3.1

1. Explain the formation of bonds in the following pairs of elements:
   a potassium and chlorine,
   b magnesium and oxygen and
   c sodium and oxygen.
2. Which of the following elements will form a ionic bond with chlorine and why? Calcium, Carbon, Oxygen and Silicon
3. Why ionic bond is also known as electrovalent bond?
4. How many types of chemical bonding you are familiar with?
5. State and explain the formation of ionic, covalent and metallic bonds. Use diagrams wherever required.
6. List four important characteristics of ionic compounds.
7. What observable properties can you use to distinguish one kind of bond from another?

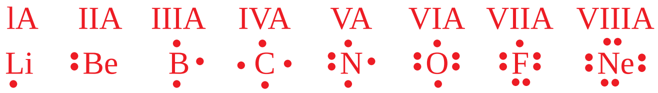
Note! Ionic compounds are usually formed when metal cations bond with non-metal anions. The only common exception is ammonium ion which is not a metal, but it forms ionic compounds.

3.2.1 Lewis Electron-Dot Symbols

In grade 9, you practiced how to write the Lewis formula for sodium and chlorine. Do their electron configurations change when these atoms form ions?

The American Chemist Gilbert N. Lewis (1875–1946) created a simple shorthand system for depicting the electrons involved in bonding and the sequence of atoms in a molecule. In a Lewis electron-dot symbol of an atom, the element symbol represents the nucleus and inner electrons, (core electrons), and it is surrounded by a number of dots equal to the number of valence electrons. You can write the Lewis symbol of any main group element from its group number (IA to VIIIA), which gives the number of valence electrons. These are placed one at a time on the four sides of the element symbol and then paired up until all are used. For example, the Lewis electron-dot symbol for phosphorus can be written as:

The Lewis electron-dot symbols for elements of period 2 may be written as:



Activity 3.5

Form a group and:

1. Use *s p d f* notation and Lewis symbols to represent the electron configuration of each of the following:

   a K^+ b S^{2-} c F^- d Al^{3+}

2. Explain how Lewis symbols and spdf notation differ in their representation of electron spin.

Share your ideas with the rest of the class.

Exercise 3.2

1. Use Lewis electron-dot symbols to depict the formation of sodium and bromide ions from the atoms and determine the formula of the compound.

2. Use Lewis electron-dot symbols to show the transfer of electrons from magnesium atoms to nitrogen atoms to form ions with noble gas electron configurations. What is the formula and name of the product?
3. Use Lewis electron-dot symbol to show the transfer of electron from aluminium to oxygen atoms to form ions with noble gas electron configurations. What is the formula and name of the product?

3.2.2 Formation of Ionic Bonding

The formation of ionic compounds is not merely the result of low ionization energies and high affinities for electrons, although these factors are very important. It is always an exothermic process; the compound is formed because it is more stable (lower in energy) than its elements. Much of the stability of ionic compounds result from the packing of the oppositely charged positive and negative ions together. A measure of just how much stabilization results from this packing is given by the lattice energy (U). This quantity is the energy change occurring when gaseous ions come together to form one mole of a solid ionic compound, or the enthalpy change required for one mole of the solid ionic substance to be separated completely into ions far removed from one another.

The lattice energy is an important indication of the strength of ionic interactions and is a major factor influencing melting points, hardness, and solubility of ionic compounds. The lattice energy plays a crucial role in ionic compound formation, but it is difficult to measure it directly. Nevertheless, the lattice energies of many compounds have been determined using Hess's law of heat summation, which states that an overall reaction's enthalpy change is the sum of the enthalpy changes for the individual reactions that make it up:

$$\Delta H_{\text{total}} = \Delta \mathrm{H}_1 + \Delta \mathrm{H}_2 + \Delta \mathrm{H}_3 + \ldots$$

Lattice energies can be calculated through a Born-Haber cycle, in which a series of steps from elements to ionic compounds for which all the change in enthalpies are known except the lattice energy. This general approach to describing the energetics of ionic compound formation is applied to sodium fluoride in the steps outlined below and illustrated in Figure 3.3.

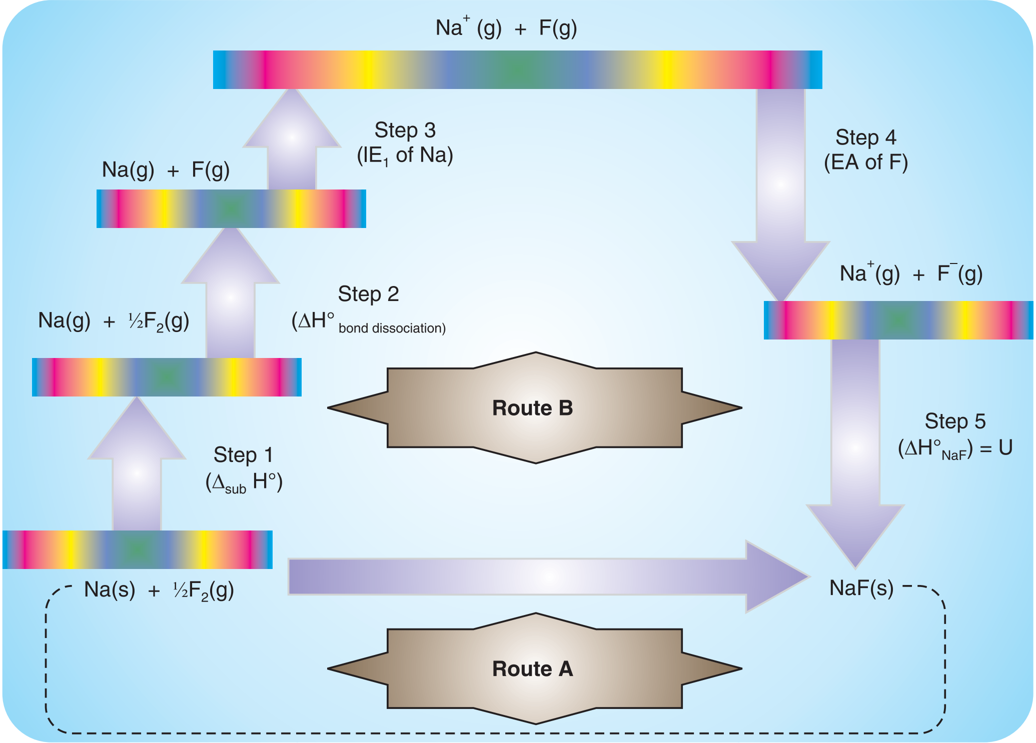


Figure 3.3 The Born-Haber cycle for NaF(s).

Consider the Born-Haber cycle for the formation of sodium fluoride. We choose steps that we can measure to depict the energy components of ionic compound formation, from which we calculate the lattice energy. We begin with the elements in their standard states, metallic sodium and gaseous diatomic fluorine. There are two routes to follow: either the direct combination reaction (Route A) or the multi-step cycle (Route B), one step of which is the unknown lattice energy. From Hess's law, it is known that both routes involve the same overall enthalpy change.

The formation of NaF(s) from its elements is shown as happening either in one overall reaction (Route A) or in five steps, each with its own enthalpy change (Route B). The overall enthalpy change for the process ($\Delta_f H^\circ$) is calculated as the sum of the enthalpy changes ΔH°_{step1}, through ΔH°_{step4}. Therefore, ΔH°_{step5}, the lattice energy (U_{NaF}), can be calculated.

$\Delta_f H^\circ$ of NaF(s) (Route A) = sum of ΔH° for steps in cycle (Route B)

To preview Route B, the elements are converted to individual gaseous atoms (Step 1 and Step 2), the electron transfer steps form gaseous ions (Step 3 and Step 4), and the ions form a solid (Step 5). We identify each ΔH° by its step number:

Step 1: Converting solid sodium to separate gaseous sodium atoms involves breaking the metallic bonds that hold atoms in the sample, so it requires energy:

$$Na(s) \rightarrow Na(g) \quad \Delta H^\circ_{step1} = +\ 108\ kJ$$

(This process is called atomization, and the enthalpy change is $\Delta_{at}H^\circ$.)

Step 2: Converting fluorine molecule to fluorine atoms involves breaking the covalent bond in F_2, so it requires energy. One mole of F atoms are needed to form one mole of NaF, so start with ½ mol F_2:

$$\frac{1}{2}F_2(g) \rightarrow F(g) \quad \Delta H^\circ_{step2} = \frac{1}{2}\text{ bond energy (BE) of }F_2$$

$$= \frac{1}{2}(154\ kJ) = 77.0\ kJ$$

Step 3: Removing the 3*s* electron from Na to form Na^+ requires energy:

$$Na(g) \rightarrow Na^+(g) + e^- \quad \Delta H^\circ_{step3} = IE_1 = +\ 495\ kJ\ mol^{-1}$$

Step 4: Adding an electron to F to form F^- releases energy:

$$F(g) + e^- \rightarrow F^-(g) \quad \Delta H^\circ_{step4} = EA = -328\ kJ$$

Step 5: Forming the crystalline ionic solid from the gaseous ions is the step whose enthalpy changes (the lattice energy) is unknown:

$$Na^+(g) + F^-(g) \rightarrow NaF(s) \quad \Delta H^\circ_{step5} = U_{NaF}\text{ (lattice energy)} = ?$$

We know the enthalpy change of the formation reaction (Route A),

$$Na(g) + \frac{1}{2}F_2(g) \rightarrow NaF(s) \quad \Delta H^\circ_{overall} = \Delta_f H^\circ = -574\ kJ$$

Therefore, we calculate the lattice energy using Hess's Law:

Solving for U_{NaF} gives

$$U_{NaF} = \Delta_f H^\circ - (\Delta H^\circ_{step1} + \Delta H^\circ_{step2}\ \Delta H^\circ_{step3} + \Delta H^\circ_{step4})$$

$$= -574\ kJ\ mol^{-1} - [108\ kJ\ mol^{-1} + 77\ kJ\ mol^{-1}$$

$$+\ 495\ kJ\ mol^{-1} + (-328\ kJ\ mol^{-1})]$$

$$= -926\ kJ\ mol^{-1}$$

Note that the magnitude of the lattice energy dominates the multistep process.

Exercise 3.3

1. Write the formulas and names of the compounds formed from the following ionic interactions: (use periodic table)
   - a The 2+ ion and 1– ion are both isoelectronic with the atoms of a chemically unreactive period 4 element.
   - b The 2+ ion and the 2– ion are both isoelectronic with the period 3 noble gas.
   - c The ions formed are the largest and smallest ionizable atoms in period 2.
2. In each of the following ionic compounds identify the main group to which X belongs:
   - a XF_2
   - b MgX
   - c X_2O_3
   - d Na_2X
3. For lithium, the enthalpy of sublimation is +161 kJ mol^{-1}, and the first ionization energy is +520 kJ mol^{-1}. The dissociation energy of fluorine is +154 kJ mol^{-1}, and the electron affinity of fluorine is –328 kJ mol^{-1}. The lattice energy of LiF is –1047 kJ mol^{-1}. Calculate the overall enthalpy change for the reaction?

   $$Li(s) \quad + \quad \tfrac{1}{2}F_2(g) \quad \rightarrow \quad LiF(s) \qquad \Delta H° = ?$$

4. The enthalpy of formation of caesium chloride is

   $$Cs(s) + \tfrac{1}{2}Cl_2(g) \quad \rightarrow \quad CsCl(s) \qquad \Delta H° = -\ 44.28\ \text{kJ mol}^{-1}$$

   The enthalpy of sublimation of caesium is

   $$Cs(s) \quad \rightarrow \quad Cs(g) \qquad \Delta H° = +\ 77.6\ \text{kJ mol}^{-1}$$

   Use these data, with other data from other sources, to calculate the lattice energy of CsCl(s)
5. Using the following data:

   Enthalpy of sublimation of Ca = +178.2 kJ mol^{-1}

   Enthalpy of dissociation of Cl_2 = +243.4 kJ mol^{-1}

   Enthalpy of formation of $CaCl_2$ = –795.8 kJ mol^{-1}

   First and second Ionization energies for Ca are +590 kJ mol^{-1} and +1145 kJ mol^{-1} respectively.

   The electron affinity of Cl = –348.7 kJ mol^{-1}

   Determine the lattice energy of $CaCl_2$

Factors Affecting Formation of Ionic Bonding

Activity 3.6

Form a group and discuss the following questions:

1. In general, how does the lattice energy of an ionic compound depend on the charges and sizes of the ions?
2. For each pair, choose the compound with the higher lattice energy, and explain your choice.

   a LiCl or CsCl b NaF or MgO c BaS or CsCl

Share your ideas with the rest of the class.

The formation of ionic bonding is influenced by various factors. Some of the major factors are presented below.

Ionization energy (IE): Elements having low IE have a more favourable chance to form a cation, thereby having a greater tendency to form ionic bonds. Thus, low ionization energy of metallic elements favours the formation of an ionic bond. That is why alkali and alkaline earth metals form ionic compounds.

Electron affinity (EA): The other atom participating in the formation of an ionic compound must form an anion by gaining electron(s) and losing energy. Higher electron affinity favours the formation of an anion. Generally, the elements having higher electron affinity favour the formation of an ionic bond. Halogens have high electron affinities, and therefore halogens generally form ionic compounds when they react with metals.

Lattice energy: When a cation and an anion come closer, they get attracted to each other due to the electrostatic (coulombic) force of attraction. The electrostatic force of attraction between oppositely-charged ions release a certain amount of energy and an ionic bond is formed. If the coulombic attraction forces are stronger, then more energy gets released and a more stable or a stronger ionic bond is formed. Larger lattice energy would favour the formation of an ionic bond. Lattice energy thus is a measure of coulombic attractive force between the combining ions. The lattice energy (U) of an ionic compound depends directly on the product of the ionic charges ($q_1 \times q_2$), and inversely on the distance (r) between them.

$$U \propto \frac{q_1 \times q_2}{r}$$

where q_1 and q_2 are the charges on +ve and –ve ions respectively, and r is the distance between the charges q_1 and q_2. Thus, small ions having higher ionic charge shall have larger lattice energy. If the total energy released is more than that which is absorbed, then the formation of ionic compound is favoured.

3.2.3 Exceptions to Octet Rule in Ionic Compounds

Activity 3.7

Form a group and discuss the following:

1. The principal exceptions to the octet rule are found in ionic compounds in which the cations do not acquire noble gas electron configuration. Identify the cations that obey or violet the octet rule.

   a $FeCl_3$ b CuO c NaCl d LiF

2. Draw Lewis structure for CH_4, BF_3 and SF_6.

   How many electrons are present around the central atoms, C, B and S, respectively?

   What is the difference between the central atoms in terms of number of electrons?

   Are these in conformity with the Octet rule?

   Can you name some more examples similar to these?

Share your ideas with the rest of the class.

As you have studied in grade 9, the octet rule works well for the representative metals (Group IA, IIA) and the nonmetals, but not for the transition elements and post-transiton elements. This is because they have d and f subshell orbitals.

There are certain exceptions to octet rule. We will discuss it here in context with the ionic compounds.

Less than Octet (Central Atom is Deficient of Electrons):

Ions of some elements which are near to helium in the periodic table do not obey the octet rule. The tendency of these atoms (H, Li, Be and B) is to attain an arrangement of two electrons like the noble gas He (duplet configuration), which is also a stable configuration. Hydride ion (H^-), lithium ion (Li^+), beryllium ion (Be^{2+}) and boron ion (B^{3+}) are isoelectronic with He. Therefore, compounds like LiH, $BeCl_2$ and BF_3 are stable in spite of short of electrons around the central atom than the octet. In these cases the number of electrons around Li, Be and B is 2, 4 and 6 respectively. Although atoms with less than an octet may be stable, they will usually attempt to form a fourth bond to get eight electrons. BF_3 is stable, but it will form BF_4 when possible.

More than Octet (18-Electron Rule):

The ions of some transition elements and post-transition elements do not usually obey the octet rule. For transition metals, the 18-electron rule replaces the octet rule, due to the involvement of d orbitals of these atoms. The atoms of these elements would have to lose a large number of electrons to achieve the noble-gas configurations. This will require enormous amount of ionization energy, which cannot be available easily. Nevertheless, these elements also form positive ions. But these ions do not have the usual noble gas valance shell electron configurations of ns^2np^6 and are not isoelectronic with any of the noble gases. It is important to note that when these atoms form positive ions, electrons are always lost first from the shells with the highest value of the principal quantum number (*n*).

Consider the electron configurations of the ions of the transition elements iron and zinc and the post-transition elements gallium and tin.

Electron Configurations of Iron:

$$_{26}\mathrm{Fe} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$$

$$_{26}\mathrm{Fe}^{2+} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$$

$$_{26}\mathrm{Fe}^{3+} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$$

A stable ion of iron with valence shell electron configuration is $3s^2\ 3p^6\ 3d^5$ which is not isoelectronic with a noble gas. Fe^{2+} is a well-known stable ion with a valence shell electron configuration $3s^2\ 3p^6\ 3d^6$ which is not isoelectronic with any of the noble gases.

Electron configurations of zinc:

Also,

$$_{30}Zn^{2+}\ :\ 1s^2\ \ 2s^2\ \ 2p^6\ \ 3s^2\ \ 3p^6\ \ 3d^{10}$$

is not isoelectronic with any of the noble gases.

Electron configurations of gallium:

The post-transition element gallium (Ga) loses electrons first from the 4p orbital and then from the 4s orbital to from a Ga^{3+} ion as

$$_{31}Ga : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$$
$$_{31}Ga^{3+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} = [Ar]\ 3d^{10}$$

On closely examining the electron configurations of Zn^{2+} and Ga^{3+}, we will realize that ions have completely-filled outer subshells and a noble gas core. Their valance electron configuration can be generally represented as $ns^2np^6nd^{10}$.

Electron configurations of tin:

The heavier post-transition elements like Pb and Sn lose the *p* electrons or both the *p* and *s* electrons from the valence shell.

$$_{50}Sn: [Kr]5s^2 4d^{10} 5p^2$$

$$_{50}Sn^{2+}: [Kr]5s^2 4d^{10}$$

$$_{50}Sn^{4+}: [Kr]4d^{10}$$

Generally, these properties are exhibited by ions of elements from

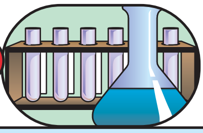
i) Group IB and Group IIB (*transition elements*) and

ii) Group IIIA and Group IVA (*heavier post-transition elements*)

Neither of these configurations are noble gas configurations.

3.2.4 Properties of Ionic Compounds

Experiment 3.1



Investigation of Solubility of Ionic Compounds

Objective: To investigate the solubility of $NaCl$ and $CuCl_2$

Apparatus and Chemicals: Test tube, water bath, Bunsen burner, $NaCl$, $CuCl_2$, ethanol, hexane and benzene

Procedure:

1. Place about 0.5 g each of $NaCl$ and $CuCl_2$ in three separate test tubes and add about 2.5 mL of water and shake well.
2. If some residue is there in the test tube/s, heat it on Bunsen burner.
3. Repeat step 1 afresh using ethanol, hexane and benzene.

   (If the salt is soluble at room temperature, do not heat it.)

Observations and analysis:

Prepare an observation table in your notebook for the solubility of $NaCl$ and $CuCl_2$ in all the three solvents at room temperature and on heating (wherever required) and record the observations.

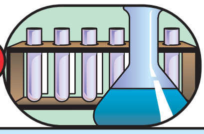
Solvent	$NaCl$	$CuCl_2$
Water		
Ethanol		
Hexane		
Benzene		

Inference/Conclusion

Interpret the observation table and give results.

Make a generalised statement about the solubility of ionic compounds in polar and non-polar solvents.

Experiment 3.2



Thermal behaviour of ionic compounds

Objective: To study the effect of heat on ionic compounds.

Apparatus and chemicals: Test tubes, test tubes holders, sodium chloride, and copper (II) chloride.

Procedure:

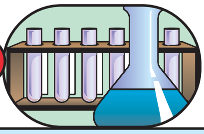
1. Take two hard glass test tubes and label them as A and B.
2. Add 0.5 g each of dry sodium chloride crystals and copper (II) chloride in test tubes A and B respectively.
3. Hold these test tubes with the help of test tube holders.
4. Heat the tubes simultaneously on the Bunsen burner flame first slowly and then strongly while shaking intermittently.

Caution: Take care not to inhale any fumes/vapours formed during heating.

Observations and analysis:

1. Do the crystals melt?
2. Do they have high or low melting points?

Experiment 3.3



Electrical Conductivity of Ionic Compounds

Objective: To test the electrical conductivity of molten compounds

Apparatus and chemicals: 9-volt battery, 6-watt bulb with a bulb holder, conducting wires, two carbon rods, lead (II) iodide or lead (II) bromide.

Procedure A:

1. Connect the circuit as shown in Figure 3.3 in which a 9 volt DC is connected via a bulb.
2. Using about 2 cm depth of PbI_2 in a small beaker, test the conductivity of the lead iodide crystals. Do not throw away the PbI_2 and be careful not to contaminate the sample because you will reuse it later. (Note: it could be

argued that a fairer test of the solid compound would be to use a lump of the compound rather than its powder).

3. Test the conductivity of large crystals of copper (II) sulphate and sodium chloride if any of them are available in your laboratory.

Procedure B:

1. Now heat the same lead (II) iodide or Lead (II) bromide (used in the above experiment) in a beaker on a tripod and wire gauze or in a boiling tube supported by a clamp and stand until it melts;
2. Test the conductivity of the molten compound by dipping the carbon electrodes (carbon rods) into the molten compound as shown in the figure below:

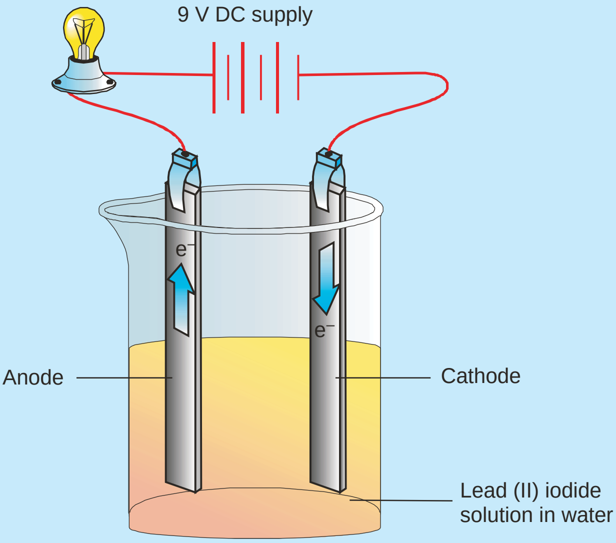


Figure 3.4 Conductivity of electrolytes.

Observations and analysis:

1. What did you observe?
2. Which of the compounds (molten or solid) conduct electricity? Why?
3. All compounds contain at least two elements. Examine the names of those compounds which conduct electricity when in molten state and decide to which classes of elements the components of these compounds belong. Name the type of bonding that exists in the compounds used.

Experiment 3.4

Electrical Conductivity of Ionic compounds

Objective: To test the electrical conductivity of the aqueous solutions of some common ionic compounds.

Apparatus and chemicals: 9-volt battery, 6-watt bulb with a bulb holder, conducting wires, two carbon rods, H_2O, lead (II) iodide, NaCl.

Procedure:

1. Dissolve the compound in 50 mL of water in two seperate beakers.
2. Connect the same circuit you used above and test the conductivity of each aqueous solution.

Observations and analysis:

a Predict what happens at the electrodes based on the type of the compound used for the experiment.

b Do you expect the same product(s) at the respective electrodes when electricity passes through molten and aqueous solutions of the compounds?

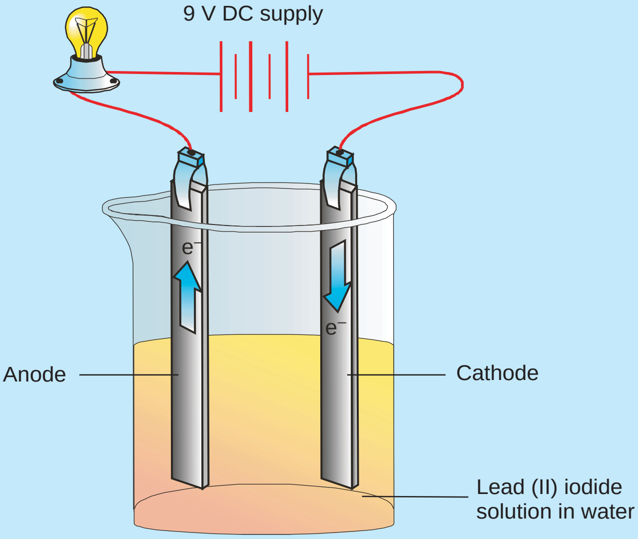


Figure 3.5 Electrochemical cell showing the conductivity of an aqueous solution.

Let us Summarise

Ionic compounds are crystalline solids at room temperature. The fundamental units of ionic solid are positive and negative ions. Crystalline ionic solids are usually brittle and non-conductors of electricity, although molten crystals may be good conductors. They usually have high melting and boiling points.

Ionic compounds are nonvolatile.

Ionic compounds are usually soluble in inorganic solvents (water is the most common solvent for ionic compounds) but insoluble in organic solvents like benzene, ethanol and carbon tetrachloride.

Note! Ionic compounds are very resistant to heat but many will be easily broken by water.

3.3 COVALENT BONDING AND MOLECULAR GEOMETRY

At the end of this section, you should be able to:

- define covalent bonding;
- explain the formation of covalent bonding;
- give examples of covalent molecules;
- draw Lewis structures or electron dot formulas of some covalent molecules;
- illustrate the formation of coordinate covalent bonding using examples;
- define resonance structures;
- draw resonance structures of some covalent molecules and polyatomic ions;
- discuss the exceptions to the octet rule in covalent bonding;
- distinguish between polar and non polar covalent molecules;
- describe the properties of covalent molecules;
- carryout an activity to investigate the effects of heat, electricity and some solvents on covalent compounds (naphthalene, graphite, iodine and ethanol);
- describe the valence shell electron pair repulsion theory (VSEPR);
- distinguish between the bonding pairs and non bonding pairs of electrons;
- describe how electron pair arrangements and shapes of molecules can be predicted from the number of electron pairs;
- explain why double bonds and lone pairs cause deviations from ideal bond angles;

- explain the term dipole moment with the help of a diagram;
- describe the relationship between dipole moment and molecular geometry;
- describe how bond polarities and molecular shapes combine to give molecular polarity;
- predict the geometrical shapes of some simple molecules;
- construct models to represent shapes of some simple molecules;
- define intermolecular forces;
- name the different types of intermolecular forces;
- explain dipole dipole interactions;
- give examples of dipole dipole interaction;
- define hydrogen bonding;
- explain the effect of hydrogen bond on the properties of substances;
- give reason why H bonding is stronger than ordinary dipole dipole interaction;
- explain dispersion (London) forces;
- give examples of dispersion forces; and
- predict the strength of intermolecular forces for a given pair of molecules;

Formation of Covalent Bonding

Activity 3.8

Form a group and attempt the following as per the instructions:

1. Give one main difference between ionic and covalent bond.
2. What happens to the valence electrons when a covalent bond is formed between two atoms?
3. Explain the formation of polar covalent and coordinate covalent bond.
4. Draw Lewis dot structures for $AlCl_4^-$ and BH_4^-.
5. Arrange single, double and triple bonds in ascending order of their bond strength and bond lengths. Justify your answer.
6. Describe the interactions that occur between individual chlorine atoms as they approach each other to form chlorine molecules (Cl_2). What combination of forces gives rise to the energy holding the atoms together and to the final internuclear distance.

Share your ideas with the rest of the class.

When elements from group IA (period 2 onwards), VIA or VIIA combine together, an ionic bond is formed. What will happen if two atoms of the same element or the elements from any of these groups combine together?

Cosider the formation of hydrogen molecule (H_2). When two hydrogen atoms are far apart, each behaves as though the other were not present. As they approach each other and the distance between the two nuclei decreases, each nucleus starts to attract the other atom's electron, which lowers the potential energy of the system. Attractions continue to draw the atoms closer, and the system becomes progressively lower in energy. As attractions increase, repulsions between the nuclei and the electrons will also increase. At some internuclear distance, maximum attraction is achieved in the face of the increasing repulsion, as the system has its minimum energy. Any shorter distance would increase repulsions and cause a rise in potential energy (see Figure 3.1). Thus, a covalent bond, such as the one that holds the hydrogen atoms together, arises from the balance between nucleus-electron attractions and electron-electron and nucleus-nucleus repulsions. Therefore, a covalent bond is formed when a pair of electrons is shared between two atoms. Some examples of covalent molecules are HCl, H_2S, C_2H_4, N_2, CCl_4, BCl_3, H_2O, NH_3, SO_2, PCl_5, O_3, etc. Generally, substances that contain covalent bonds are called molecules.

Note: Ionization energy of hydrogen (IE_1 = 1312 kJ mol^{-1}) is very high making it difficult to lose electron.

Representation of Covalent Bond (Drawing Lewis Structures)

The representation of covalent bonding through Lewis symbols and shared electron-pairs is called a Lewis structure. Lewis structure for hydrogen molecule formed from hydrogen atoms is

$$H\bullet + \bullet H \rightarrow H{:}H$$

If we "double count" the shared electrons each H atom appear to have two electrons in its valence shell analogous to the electron configuration of helium.

Similarly, consider fluorine, which also exists in the diatomic form, F_2. Fluorine atoms are also joined by a covalent bond.

Each fluorine atom in the fluorine molecule has eight valence electrons, an arrangement lsimilar to that of the noble gas argon. The fluorine atoms obey the octet rule. The shared pairs of electrons in a molecule are called bonding pairs. The other electron pairs that stay with on atom and are not shared are called non-bonding pairs or lone pairs.

We can write the Lewis formula for a convalent compound of known geometry by using the following rules.

1. Determine the total number of valence electrons. It is this number of electrons that must appear in the final Lewis structure. The total number of electrons for a molecule is the sum of the valence electrons for each atom. For a polyatomic anion, which has one or more extra electrons, add one electron for each unit of negative charge. For a polyatomic cation, which is missing one or more electrons, subtract one electron for each unit of positive charge.

Exercise 3.4

Determine the total number of valence electrons for the following species:

a CO_2

b SO_4^{2-}

c NH_4^+

d N_2O_4

2. Write the skeletal structure. The most electropositive atom usually occupies the central position. Connect bonded atoms with an electron-pair bond (a dash). Hydrogen is an exception; it is always a terminal atom, even when bonded to a more electronegative atom.

3. Place electron pairs around terminal atoms so that each (except hydrogen) has an octet.

4. Assign any remaining electrons as lone-pairs around the central atom.

5. If at this stage, a central atom has fewer than eight electrons, a multiple bond(s) is likely. Move one or more lone-pair of electrons from a terminal atom(s) to a region between it and the central atom to form a double or a triple bond.

Exercise 3.5

1. Write a plausible Lewis structure of:
   - a nitrogen trichloride, NCl_3
   - b chlorate ion, ClO_3^-
   - c phosphonium ion, PH_4^+
   - d phosgene, $COCl_2$
2. Draw a Lewis structure for CO_3^{2-}, SF_4 and HCOOH (formic acid).
3. Which of the following atoms cannot serve as a central atom in a Lewis structure O, He, F, H, P? Explain.
4. Write a plausible Lewis structure for carbonyl sulphide, COS.

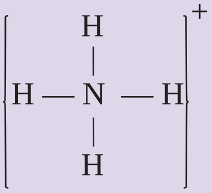
Coordinate-Covalent Bonding

What is a coordinate covalent bond?

Activity 3.9

Form a group and discuss the following:

1. Why (a) the ammonia molecule, (b) the oxygen atom can participate readily in coordinate covalent bonding.
2. Use Lewis structures to show the formation of coordinate covalent linkage between (a) phosphorus trichloride and oxygen (b) boron trifluoride and ammonia.
3. In the following structure of ammonium ion, can you identify the coordinate covalent bond?



$$\left[\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{N}-\text{H} \\ | \\ \text{H} \end{array}\right]^{+}$$

Share your ideas with the rest of the class.

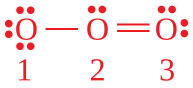
Covalent bonds are formed through the contribution of one electron each by atoms involved in an electron-pair bond. There is another possibility in which one atom can "donate" two of its electrons to provide the shared pair between itself and an "acceptor" atom. When one atom provides both the electrons for a shared pair, the bond is called a coordinate-covalent bond.

Some examples of molecules which contain coordinate-covalent bond include O_3, NH_3BF_3 and $POCl_3$.

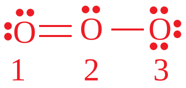
Resonance Structures

Discuss the concept of resonance. What is the difference between a resonance structure and a resonance hybrid?

For some molecules, there is no best choice between a number of equally acceptable Lewis structures. Consider the simple example of ozone, O_3, in which the arrangement of nuclei is O–O–O. This molecule has $6 \times 3 = 18$ valence electrons, and it is possible to draw two possible structures for O_3:

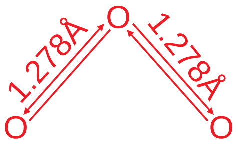


(I)

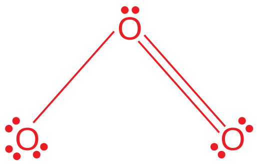


(II)

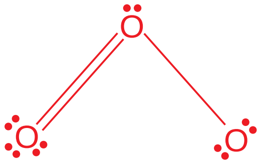
Both the structures satisfy octet rule. The two structures for O_3 suggest that the bond between O^1 and O^2 differs from that between O^2 and O^3 one single bond and one double bond. Therefore, in each of the two structures one bond should be a single bond while the other a double bond. If it is so then one bond (double bond) should be shorter than the other bond (single bond). But experimental evidences show that both the bonds are exactly equivalent having same bond lengths and bond strengths.



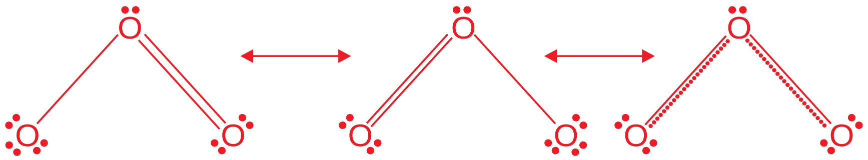
Since both the bonds are identical which one is a double bond?



or



The Lewis structure is equivalent except for the placement of the electrons (i.e., the location of the double bond). In such a situation, the correct way to describe ozone molecule as Lewis structures would be:



Resonance Structures

Resonance Hybrid

This indicates that the ozone molecule is described by an average of two Lewis structures (i.e. the resonance forms). The bond-lengths between the oxygens are intermediate between characteristic single and double bond-lengths between a pair of oxygen.

This description of O_3 is called resonance, a circumstance in which two or more possible Lewis structures can be written and the true structure is a composite or hybrid of them. The different structures used to represent the molecule or ion are called contributing structures or resonance structures, and we write them linked by double-headed arrows. The actual species that exists is called a resonance hybrid. The resonance structures differ only in the distribution of electrons.

Known misconceptions about the structure of ozone:

- The bond lengths between the central oxygen and the other two oxygen atoms are identical.
- It may be expected that if one bond is a double bond, then it should be shorter than the other (single) bond.

In molecules such as CH_4, H_2S, NF_3, PF_5, SF_6 etc in which resonance is not involved, bonding electron pairs can be described as existing in fairly well-defined regions between the two atoms. These electrons are localized. In O_3, to produce O-to-O bonds that are intermediate between single and double bonds, we need to think of some of the electrons in the resonance hybrid as being delocalized. Delocalized electrons are bonding electrons that are spread over several atoms.

Activity 3.10

Form a group and discuss the concept of resonance. When is this concept applied to depict adequately the bonding in a molecule; explain using suitable examples.

Share your ideas with the rest of the class.

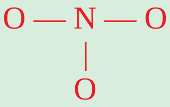
Example 3.1

Write three equivalent Lewis structures for the nitrate ion, NO_3^-. Describe its resonance hybrid structure.

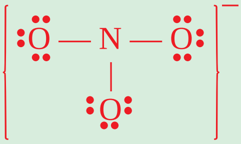
Solution:

a There are 5 + (3 × 6) + 1 = 24 electrons

b The skeletal structures is:

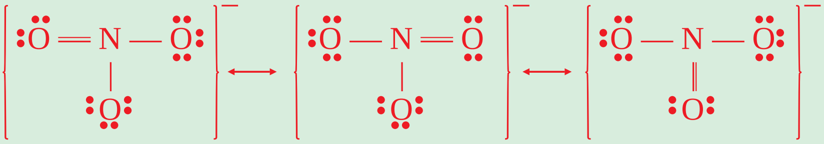


c Place three lone pairs of electrons on each O atom.



d All 24 electrons have been assigned.

e The central N atom has only six valence electrons as shown. Move a lone pair of electrons from one of the terminal oxygen atom to from a double bond to the central N atom. Because the double bond can go to any one of the three O atoms, we get three structures that differ only in the position of the double bond.



The resonance hybrid, which involves equal contributions from these three equivalent resonance structures, has N-to-O bonds with bond length and bond energies intermediate between single and double bonds.

Exercise 3.6

1. Write three equivalent structures for the SO_3 molecule that obey the octet rule.
2. Draw Lewis structures of all the important resonance forms of each of the following:

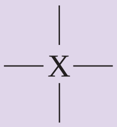
   a NO_2F(N central) b HNO_3 c NO_2^-

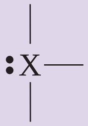
Exceptions to the Octet rule in Covalent Bonding

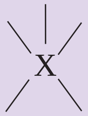
Activity 3.11

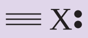
Form a group and discuss the following questions:

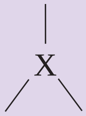
1. In which pattern(s) does X obey the octet rule?

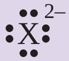
a 

b 

c 

d 

e 

f 

2. What requirements are needed for an atom to expand its valence shell? Which of the following atoms can expand its valance shell; F, S, H, Al?

3. Identify the atoms in PCl_3, PCl_5, OF_2, BF_3, and SiF_4 which do not obey octet rule.

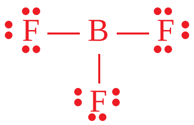
Share your ideas with the rest of the class.

It has been noticed that there are three groups of molecules that are exceptions to the octet rule.

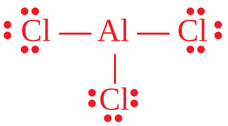
Less than octet (central atom is deficient of electrons):

Molecules whose central atoms have fewer than eight electrons (Below octet). This group consists of molecules containing central atoms from Group IIA and IIIA. $BeCl_2$, BF_3 and $AlCl_3$, whose Lewis formula are shown below, are typical examples:

4 electrons around Be



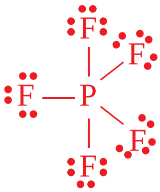
6 electrons around B



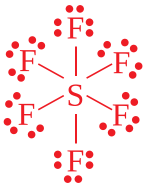
6 electrons aroud Al

More than octet (central atom has excess of electrons):

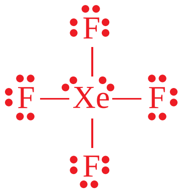
Molecules whose central atoms have more than eight electrons (Expanded octet). This group consists of molecules containing central atoms from periods 3, 4, 5, and 6. PF_5, SF_6 and XeF_4 are typical examples of this type;



10 electrons around P



12 electrons around S



12 electrons aroud Xe

Molecules containing an odd number of electrons:

Even if stable molecules of this kind are rare, they do exist. Some examples are ClO_2, NO and NO_2 having 19, 11 and 17 valence electrons respectively. The best way to suggest the Lewis-like structure for these molecules is:

ClO_2

Exercise 3.7

1. Suggest the Lewis-like structure for NO and NO_2 molecules.
2. The following species do not obey the octet rule. Draw a Lewis structure for each one and state the type of octet rule exception:

   a BH_3　b AsF_4^-　c $SeCl_4$　d PF_6^-

   e ClO_3　f BrF_3　g BeF_2　h XeF_2

Polar and Non-Polar Covalent Molecules

Activity 3.12

From a group and collect the following substances. Divide them in two groups. Group A consists of:

a Naphthalene
b Sodium chloride
c Iodine
d Wax

and group B consists of the following solvents

i Carbon tetrachloride
ii Water
iii Methylbenzene

Each solid in group A dissolves best in at least one solvent in group B. Point out the solid and the solvent it dissolves in and give reasons for your choice.

When bonding electron-pairs in a covalent bond are shared equally, the result is a nonpolar covalent bond. When the atoms are alike in a covalent bond, the two atoms with equal electronegativities will exhibit equal sharing of an electron pair, and the electrons are not drawn closer to one atom than to the other. The H–H and Cl–Cl bonds are nonpolar. In a covalent bond between atoms of different electronegativities, there is an unequal sharing of an electron pair and the electrons spend more of their time around the more electronegative atom. Such a bond is said to be polar covalent bond. The H–Cl bond is a polar bond. This is because chlorine is more electronegative than the hydrogen atom and represented as

$$H^{\delta +} - Cl^{\delta -}$$

to indicate the polar nature of a bond. In the representation the $\delta+$ and $\delta-$ (read "*delta plus*" and "*delta minus*") signify that one end (H) is partially positive and the other end (Cl) is partially negative. The term partial charge signifies something less than the full charges of the ions that would result from complete electron transfer.

For a diatomic molecule having a polar covalent bond, such as HCl, we can describe a quantity called the dipole moment, which is a vector sum of the bond moments in a molecule. Bond moment is a measure of polarity of a diatomic covalent bond. The dipole moment (μ) is defined as the product of the magnitude of the charge (δ) at either end of the dipole multiplied by the distance (d) that separates the charge.

$$\mu = \delta \times d$$

The SI-unit of dipole moment is coulomb-metre (C.m). Dipole moments are often expressed in the non-SI unit debye (D), where $1D = 3.33564 \times 10^{-30}$ Cm.

Note! For a diatomic molecule, the bond moment is the dipole moment. The dipole moment of a polyatomic molecule (three or more atoms) depends on the geometry of the molecule. If the bond moments are equal in magnitude but opposite in direction, then they will cancel each other and the resultant dipole moment will be zero, provided that the vector sum of the bond moments is zero.

Exercise 3.8

Both CO_2 and BCl_3 have zero dipole moments, but the C = O and B – Cl bond moments are not zero. Explain.

Properties of Covalent Compounds

Tetrachloromethane (carbon tetrachloride) is a covalent compound. Would you expect it to be a conductor of electricity?

Experiment 3.5

Investigating the effect of heat on covalent compounds

Objective: To determine the melting points of naphthalene.

Apparatus and chemicals: Thermometer, stirrer, beaker, melting point tube, naphthalene, glycerine, Bunsen burner.

Procedure:

Set up the apparatus shown in Figure 3.6. Place a small amount of naphthalene in melting point tube. Attach the tube to the side of the thermometer (the liquid in the beaker will hold the tube in position). Heat the beaker slowly. When the naphthalene melts, record the reading on the thermometer. Determine the melting point of iodine and graphite similarly.

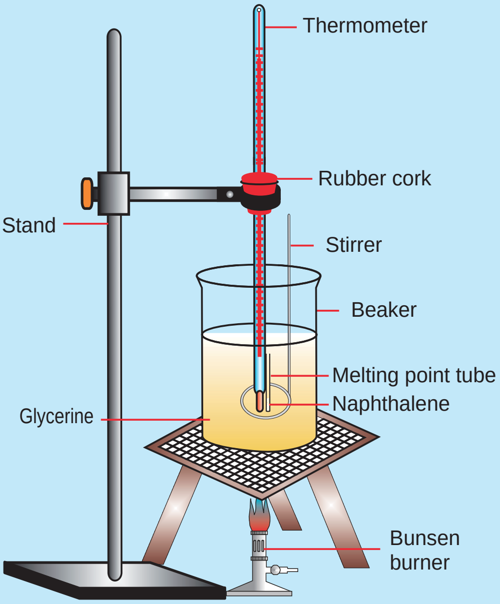


Figure 3.6 Determination of melting point of naphthalene.

Observations and analysis:

Check your result by referring to standard melting point values. Discuss on possible reasons for the differences in melting point compared to the standard melting point.

Experiment 3.6

The effects of heat, electricity and some solvents on covalent compounds

Objective: To test the effects of heat, electricity and some solvents on covalent compounds.

Apparatus and chemicals: Beakers, stirrer, test tubes, water, alchohol, naphthalene, iodine crystals, and graphite.

Procedure:

You are provided with four substances, namely naphthalene, graphite, iodine and ethanol. Investigate the effect of heat and electricity on these substances as well as their solubility in water and other non-polar (organic) solvent.

Observations and analysis:

Record your observations in the following table by drawing on your note book.

Substance → Property ↓	**Naphthalene**	**Graphite**	**Iodine**	**Ethanol**
Effect of Heat				
Effect of Electricity				
Solubility in water				
Solubility in non-polar solvent				

Results and Discussion:

1. Draw your conclusion from the above observations.
2. Do these substances conduct electricity either in the solid state or in the molten (liquid) state?
3. Is there any chemical reaction that takes place at the electrodes?

Activity 3.13

Form a group and discuss the following question:

Why does ammonia, NH_3, dissolve in water but methane, CH_4 does not?

Share your ideas with the rest of the class.

Unlike any ionic compound, many of the covalent compounds are found in gaseous state at room temperature. Consider methane (CH_4), the simplest compound between carbon and hydrogen, which have comparable, intermediate electronegativities. It is a gas at room temperature. Cooling methane to a low temperature condenses it first to a liquid and then to a solid. Unlike melted ionic compounds, liquid covalent compounds do not conduct electricity. Therefore, liquid methane does not conduct electricity. Covalent compounds are molecular substances. They have low melting and boiling points. Most covalent compounds are soluble in non-polar solvents. Generally,

- Covalent compounds exist as separate molecules because electrically neutral atoms form them and the forces of attraction between these molecules are relatively weak.
- Due to weak intermolecular forces, many covalent molecules or covalent compounds are liquids or gases at room temperature. However, some covalent molecules like iodine are solids at room temperature.

Liquid — H_2O, Br_2,
Gas — CO_2, H_2, Cl_2, NH_3.

- Covalent compounds are volatile.
- Generally they have low melting points and boiling points.
- Covalent compounds are generally insoluble in water. Most covalent compounds are soluble in nonpolar solvents.
- Nonpolar covalent compounds are non-electrolytes because they do not conduct electricity.

3.3.1 Molecular Geometry

Valence Shell Electron Pair Repulsion (VSEPR) Theory

A molecule is an independent, minute architecture extending in three dimensions throughout its tiny volume of space. Let us discuss the shapes of molecules and their effect on the properties of a molecule. We start by describing the Valence Shell Electron Pair Repulsion (VSEPR) model, which allows us to convert two-dimensional Lewis structure into three-dimensional (3D) geometry.

The basic principle of VSEPR theory is that the pair of valence shell electrons around the central atom stays as far apart from each other as possible to minimize repulsion among them. For simplicity, a set of electrons is defined as any number of electron-pairs that occupies a localized region around a central atom. This set may consists of a single bond (–), a double bond (=), a triple bond (≡), lone-pair(s) or in some cases even a lone (single) electron. Each of these is a separate set of electrons that repels the other groups and occupies as much space as possible around the central atom - one set of electrons repels the other sets to maximize the angles between them. The three-dimensional arrangement of these sets gives rise to the shape of the molecule.

Electron Pair Arrangement and Molecular Shape

The electron pair arrangement is defined by the sets of electrons, both bonding and nonbonding (lone-pair), around the central atom. On the other hand the molecular shape is defined by the relative positions of the atomic nuclei. Molecular shapes that occur when all the surrounding electron sets are bonding sets differ from molecular shapes when some of the electron sets are non-bonding sets. Thus, the same electron set arrangement can give rise to different molecular shapes. To classify molecular shapes, the AX_mE_n designation is assigned, where A is the central atom, X is the terminal atom, E is lone-pair (nonbonding) electron sets, m and n are positive integers.

The arrangements that best minimize repulsions naturally depend on the number of electron sets. Repulsive forces among valence pairs diminish in the following order:

Lone pair vs lone pair > lone pair vs bonding pair > bonding pair vs bonding pair.

In this section, you will see electrons set ranging from two to six around the central atom. Two electron sets locate themselves on opposite sides of the atom in a linear arrangement, three sets form a trigonal planar structure, four sets arrange themselves at the corners of a tetrahedron, five sets define a trigonal bipyramid, and six sets form an octahedron.

In the case of multiple (*double or triple*) bonds the counting is not different, because you are already informed that a double bond is considered as one set and a triple bond as another set of electrons. For example, in the case of CO_2, O=C=O, there are two sets of electrons around the central atom, acetylene, C_2H_2, H–C≡C–H, two sets of electrons around each of the central atoms.

Guidelines for Applying VSEPR Model

The VSEPR model is an approach of using the number of electrons surrounding a central atom to study the molecular structures, based on the theory that the structure around a given atom is determined principally by minimizing electron-pair repulsion. Here are some guidelines for applying the VSEPR model:

1. First, write the Lewis structure of the molecule, in this model, consider only the electron sets (pairs) of the central atom.
2. Count the total number of electron sets around the central atom, including both the bonding pairs and lone pairs. Usually a lone pair, a single unpaired electron and any bond: single, double or triple, each count as one area of electron density. For species with more than one central atom, treat each central atom separately.
3. Use the VSEPR geometry to predict the shape of the molecule.
4. In predicting bond angles, bear in mind that the repulsion of the lone pairs is stronger than between those of the bonding pairs. VSEPR theory is best used as a tool to explain why a given structure is distorted rather than as a predictive tool.

In explaining why the distortion occurs you need to balance three competing influences:

- lone pairs take up more space than bonding pairs. Repulsions between electrons in a lone-pair and the other electrons (in either bonds or other lone pairs) may cause distortions in the structure.
- triple bonds are fatter than double bonds, which are fatter than single bonds. The amount of electron-electron repulsion experienced between a bond and lone pairs or other bonding pairs decreases in the order: triple > double > single. Therefore, we expect that a triple bond may cause more distortions in the structure than either a double or single bond and that a double bond will cause more distortion when compared to a single bond.
- bonds which involve a significant difference in electronegativity between the atoms in the bond will have the electrons in the bond distorted toward the more electronegative atom. This will decrease electron density near the central atom and lessen the repulsion between this bonding-pair and other electron-pairs in the molecule.

Molecular Shape and Molecular Polarity

Activity 3.14

Form a group and discuss the following:

Water has a resultant dipole moment of 6.23×10^{-30} C m(1.87D). Explain why this fact proves that the H_2O molecule must have a bent shape.

Share your ideas with the rest of the class.

Many aspects of molecule's chemical behaviour can be understood if one knows the geometry (*shape*) of a substance. Molecular shape affects many properties of the molecule like molecular polarity, which in turn influence melting and boiling points, solubility, and even reactivity. Molecular polarity is created by molecules with a net imbalance of charge. In molecules with more than two atoms, both shape and bond polarity determines the molecular polarity.

Bond Polarity and Dipole Moment

Activity 3.15

Form a group and discuss the following questions:

There are three different dichloroethenes, $C_2H_2Cl_2$, which we can designate *x*, *y* and *z*. Compound *x* has no dipole moment, but compound *z* does. Compound *z* and *x* each combine with hydrogen to give the same product:

$$C_2H_2Cl_2 + H_2 \rightarrow ClCH_2 - ClCH_2$$

(x or z)

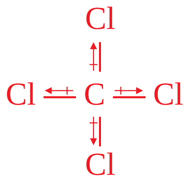
What are the structures of *x*, *y* and *z*? Would you expect compound *y* to have a nonzero dipole moment?

Share your ideas with the rest of the class.

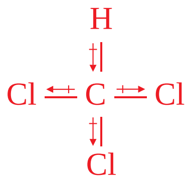
Polar bonds do not necessarily lead to polar molecules. For example, the large electronegativity difference between C and oxygen makes each C-O bond quite polar. However, because carbon dioxide (CO_2) is a AX_2 type molecule with two sets of electrons around the central atom, and its shape is linear, and its bonds are directed 180° from each other, so there is no net dipole moment (μ); $\mu = 0$ D

Another molecule with identical atoms bonded to the central atom is water. Unlike carbon dioxide, water has a significant dipole moment ($\mu = 1.87$ D). Both water and carbon dioxide are triatomic molecules and you may expect them to exhibit similar shape and polarity. Due to the effect of the lone pairs of electrons on its shape, water is a polar molecule. In each O–H bond, electron density is pulled toward the more electronegative O atom, but the bond polarities do not counterbalance each other, because the water molecule is V-shaped. Instead, the bond polarities partially reinforce each other, and the oxygen end of the molecule is considerably more negative than the other end.

Carbon dioxide and water demonstrate how molecular shape influences polarity. When two or more different molecules have the same shape, the nature of the atoms surrounding the central atom can have a major effect on the polarity of a molecule. Consider tetrachloromethane (CCl_4) and trichloromethane ($CHCl_3$), two AX_4 type molecules - tetrahedral shape with different polarities. In CCl_4, the surrounding atoms are all Cl atoms. Although each C–Cl bond is polar, the molecule is nonpolar because the individual bond polarities counterbalance each other. In $CHCl_3$, an H atom substitutes for one of the Cl atoms, disturbing the balance and giving chloroform a significant dipole moment.

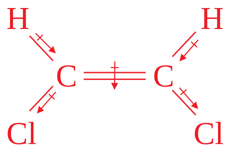


$\mu = 0\ D$

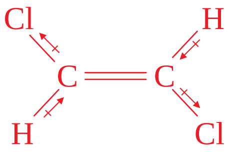


$\mu = 1.02\ D$

If you consider the two constitutional isomers of dichloroethane ($C_2H_2Cl_2$), they have the same molecular formula. However, they have different physical and chemical properties. VSEPR theory predicts that all the nuclei lie in the same plane with a trigonal planar molecular shape around each carbon atom.



Cis



Trans

The trans isomer has no dipole moment ($\mu = 0$ D) because the C – Cl bond polarities balance each other. In contrast, the cis-isomer is polar ($\mu = 1.90$ D) because the bond dipoles partially reinforce each other, with the molecular dipole pointing between the Cl atoms.

Bond Angle

Bond angle is the angle formed by two surrounding atoms with the central atom at the vertex. Ideal bond angles are observed when all the bonds around a central atom are identical and connected to the same type of atom. When this is not the case, such as when lone pairs, multiple bonds, or different surrounding atoms are present, the bond angles deviate from the ideal angles.

Predicting the Shapes of Molecules

The geometrical shapes of some simple molecules can be predicted based on the following general patterns:

Molecular Shapes with Two Electron Sets (Linear Arrangement-AX_2 type)

The repulsion of two electron groups with each other results in the assignment on opposite sides of the central atom in a straight line. The linear arrangement of electron sets results in a linear molecular shape and bond angle of 180°. All AX_2 type molecules or ions are linear in geometry. The examples of the molecules of this type are CO_2, $BeCl_2$, CS_2, HCN, etc.

Molecular shapes with three electron sets (Trigonal Planar Arrangement, AX_3 type)

Three electron sets around the central atom repel each other to lie at the corners of an equilateral triangle. This is the trigonal planar arrangement and the ideal bond angle is 120°: Example: BF_3, NO_3^-, HCHO (formaldehyde) etc. Another molecular shape is possible within this electron set arrangement, with two bonding and one lone pair (AX_2E type). The examples of this type include $PbCl_2$, $SnBr_2$, SO_2, O_3, etc. They have bent (V-*shaped or angular*) geometry. This is the first example of the effect of a lone-pair on adjacent bonding-pairs. Since a lone-pair is held on the central atom, it exerts a stronger repulsion than bonding pair.

Thus, in AX_2E type species a lone-pair repels bonding-pairs more strongly than bonding-pairs repel each other. The repulsion increases the angle between lone-pair and bonding-pair, which decreases the angle between bonding-pairs. Note the large decrease from the ideal 120° angle in AX_2E type molecules. (Example $SnCl_2$ = 95°).

Molecular Shapes with Four Electrons Sets (Tetrahedral Arrangement, AX_4 Type)

Note that AX_3E and AX_2E_2 types are with four electron sets like AX_4 type but differ in shape and bond angle because of the presence of lone pair(s) on the central atom.

In three dimensions, the four electron sets can move farther apart and point to the corners of a tetrahedron, giving a bond angle of 109.5º. Therefore, all molecules or ions with four electron sets around the central atom adopt the tetrahedral arrangement. Some of the examples of this type are CH_4, NH_4^+, SO_4^{2-}. When one of the four electron sets in the tetrahedral arrangement is a lone pair, the molecular shape is that of a triagonal pyramid (AX_3E type). The measured bond angle is slightly less than the ideal 109.5°. In ammonia (NH_3), for example, the lone pair forces the N–H bonding pairs together, and the H–N–H bond angle is 107.3°. When the four sets of electrons around the central atom include two bonding and two non-bonding sets, the molecular shape is bent, V-shaped or angular (AX_2E_2 type). Recall that one of the shapes in the triagonal planar arrangement - that with two bonding sets and one lone pair-is also called angular or bent or V-shaped (AX_2E type), but it is ideal bond angle is 120°, not 109.5°. Water is the most important V-shaped molecule in the tetrahedral arrangement of electrons. We would expect the repulsions between its two lone-pairs have a greater effect on bond angle than the repulsions from the single lone pair in NH_3, and observation confirms this: two lone-pairs on the central O atom compress the H–O–H bond angle to 104.5°.

Thus, for similar molecules within a given tetrahedral electron set arrangement, electron pair repulsions cause deviation from ideal bond angles.

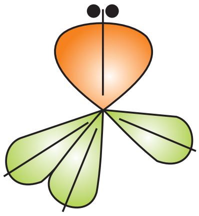


Figure 3.7 Molecular shape of ammonia.

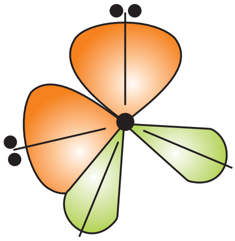


Figure 3.8 Molecular shape of water.

Example 3.2

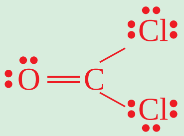
Determine the molecular shape of and ideal bond angles in:

1. $COCl_2$
2. PCl_3
3. SF_2

Solution:

1. For $COCl_2$

   a Write the Lewis Structure



   b Assign the electron set arrangement: There are three sets of electrons around carbon (*two single and one double bond*) gives AX_3 type molecule with a trigonal planar arrangement of electron sets.

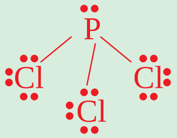
   c The ideal bond angle is 120°.

   d The shape is trigonal planar.

   The correct Lewis structures determine the other steps. Therefore, you have to be sure when you sketch the structure.

2. For PCl_3

   a Write the Lewis structure:



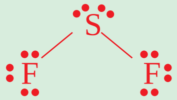
   b Assign the electron set arrangement. There are four electron sets around phosphorus (three bonding and one lone pair) gives AX_3E type, a molecule with tetrahedral arrangement of electron sets.

   c The ideal bond angle is 109.5°. Since there is one lone pair, the actual bond angle should be less than 109.5°.

   d PCl_3 has a trigonal pyramidal shape.

3. For SF_2

   a Write the Lewis structure:

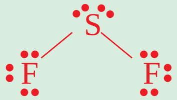


   b Assign the electron set arrangement:

   There are four electron sets around sulphur (two bonding and two lone pair) give AX_2E_2 type, a molecule with tetrahedral arrangement of electron sets.

   c The ideal bond angle is 109.5°. Since there are two lone-pairs, the actual bond angle should be less than a tetrahedral arrangement of electron sets with one lone-pair.

   d SF_2 has angular (*bent*) or V-shape.



Exercise 3.9

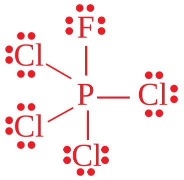
Determine the molecular shape and ideal bond angles in

a SO_4^{-2} b CS_2 c H_2Se

Molecular Shapes with Five Electron Sets (Trigonal Bipyramidal Arrangements, AX_5 Type)

AX_4E, AX_3E_2 and AX_2E_3 types are with five electron sets around the central atom like AX_5 type but differ in shape and bond angle because of the presence of one or more lone-pairs on the central atom. Therefore, we dare to predict that the electron set geometry is trigonal bipyramidal.

Molecules with five or six electron sets must have a central atom from period 3 or higher with *d*-orbitals available to expand its valence shell beyond eight electrons. When five electron sets maximize their separation, they form the trigonal bipyramidal arrangement with all five positions occupied by bonded atoms, the molecule has a trigonal bipyramidal shape (AX_5 type). Phosphorus pentachloride (PCl_5) is an example:



Lone-pairs exert stronger repulsive forces than bond pairs. With one lone-pair present (AX_4E type), the molecule has a Seesaw shape. For example, SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$. With two lone pairs present (AX_3E_2 type), the molecule has a T-Shape. Some of the examples of this type include ClF_3, BrF_3, and ICl_3.

Molecules with two bonding and three lone pair sets are linear in shape (AX_2E_3 type). The examples of this type are XeF_2, I_3^-, IF_2^-.

Molecular Shapes with Six Sets of Electrons (Octahedral Arrangement, AX_6 Type)

AX_5E and AX_4E_2 are the two common shapes under consideration. They are with six sets of electrons like AX_6 type and exhibit similar electron arrangement around the central atom but different molecular shapes.

With six bonding groups, the molecular shapes are octahedral (AX_6 type). For example, SF_6, IOF_5. Five bonded atoms and one lone pair (AX_5E type) define the square pyramidial shape. The examples of this type are BrF_5, TeF_5^-, $XeOF_4$.

When a molecule has two lone pairs and four bonding set (AX_4E_2 type) the positioning gives rise to the square-planar shape. The examples of this type are XeF_4, ICl_4^-

Exercise 3.10

1. In which situation/s the molecular shape and the electron-set arrangement is/are same?
2. Arrange the following AF_n species in order of increasing F–A–F bond angles. BF_3, BeF_2, CF_4, NF_3, OF_2
3. In the gas-phase, phosphorus pentachloride exists as separate molecules. In the solid phase, however, the compound is composed of alternating PCl_4^+ and PCl_6^- ions. What change(s) in molecular shape occur(s) as PCl_5 solidifies? How does the angle change?
4. For molecules of general formula AX_n (where $n > 2$), how do you determine if a molecule is polar?
5. For each of the following molecular formula (AX_mE_n), A is the central atom, X is the terminal atom, *m* is the number of terminal atoms bonded to the central atom; E is the lone-pair of electrons and *n* is the number of lone-pairs possessed by the central atom. The first item has been completed as an example. Fill the rest of the table after drawing in your note book.

Number of e-pairs	**Molecular formula**	**Molecular geometry**	**Electron set geometry**	**Sketch**	**Examples**
2	AX_2	linear	linear	X–A–X	Cl–Be–Cl
3	AX_2E AX_3				
4	AX_4 AX_3E AX_2E_2				
5	AX_5 AX_4E AX_3E_2 AX_2E_3				
6	AX_6 AX_5E AX_4E_2				

6. Determine the molecular shape and predict the bond angles (relative to the ideal angles) in

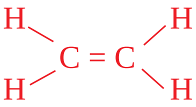
   a SbF_5 b BrF_5

7. Predict the geometry of and bond angles (relative to the ideal angles) in the following molecules and ions.

   a ClO_3^+ b ClO_2^+ c ICl_2^- d SOF_4 e ClF_3

8. Draw molecular shapes for the molecules/ions in question number 8.

The molecular shape of molecules with more than one central atom are different in defferent parts of the molecule. Consider ethene (C_2H_4). Three bonding sets and no lone pair are around each of the two central carbon atoms, so ethene is shaped like two trigonal planar geometries that share a point.



Ethanol (CH_3CH_2OH) has three central atoms. The CH_3 group is tetrahedrally shaped and the CH_2 group has four bonding groups around its central C atom, so it is also tetrahedrally shaped. The O atom has four sets of electrons, but the two lone pairs give it a V-shape (AX_2E_2 type). For these types of molecules, it is easiest to find the molecular shape around one central atom at a time. Figure 3.8 is another example for the molecular shape of molecules with more than one central atom.

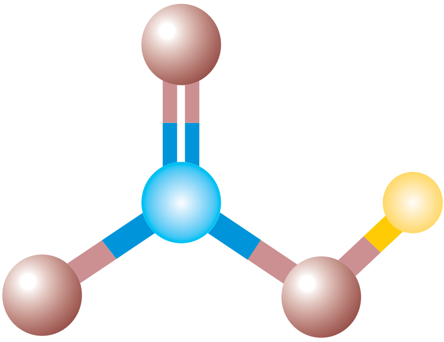


Figure 3.9 Predicted geometrical shape of the HNO_3 molecule by the VSEPR theory.

3.3.2 Intermolecular Forces in Covalent Compounds

Activity 3.16

Form a group and discuss the following questions:

1. Why does a polar liquid generally have a higher normal boiling point than a nonpolar liquid of the same molecular mass?
2. State the principal reasons why CH_4 is a gas at room temperature whereas H_2O is a liquid.
3. Only one of these substances is a solid at STP: C_6H_5COOH, $CH_3(CH_2)_8CH_3$, CH_3OH, $(CH_3CH_2)_2O$. Which do you think it is and why?
4. Only one of these substances is a gas at STP: NI_3, BF_3, PCl_3, and CH_3COOH. Which do you think it is and why?

Share your ideas with the rest of the class.

There are two types of electrostatic forces at work in any sample of matter. These are: intramolecular and intermolecular forces. Intramolecular force which is a chemical bond (ionic, covalent or metallic) is a force that exists within a particle (molecule or polyatomic ion) and affects the chemical property of the species. Whereas, intermolecular forces exist between particles and influence physical properties of the species

Intermolecular forces are due to the attraction between ions and molecules. Intermolecular forces are relatively weak as compared to intramolecular forces, because they typically involve lower charges that are farther apart. The charges that give rise to intermolecular forces are farther apart because they exist between non-bonded atoms in adjacent molecules.

Activity 3.17

Form a group and discuss the following:

1. Name some intermolecular forces.
2. Cis-1,2-dichloroethene shows higher boiling point than trans-1,2 dichloroethene. Explain.
3. Which type of compounds exhibit hydrogen bonding?
4. Name the factors on which the strength of dispersion forces of the particles depend?
5. 'Ice is lighter than water.' Comment

Share your views with rest of the class.

Though there are several important types of intermolecular forces, only dipole-dipole, hydrogen bonding, and, London (Dispersion) forces, will be discussed.

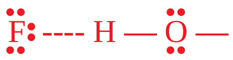
Dipole-Dipole forces

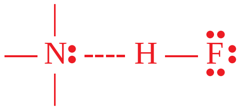
When polar molecules are brought near one another, their partial charges act as tiny electric fields that orient them and give rise to dipole-dipole forces; the partially positive end of one molecule attracts the partially negative end of another.

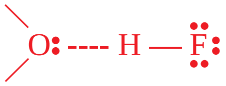
For compounds of approximately the same mass and size, greater is the dipole moment, greater is the dipole-dipole forces between their molecules, so greater is the energy required to separate their particles. These can be manifested in several of its physical properties. For instance, both methyl chloride (CH_3Cl) and ethanal (CH_3CHO) have comparable mass and size, but CH_3Cl has a smaller dipole moment than CH_3CHO; therefore less energy is needed to overcome the dipole-dipole forces between its molecules and it boils at a lower temperature. Dipole-dipole forces give polar cis-1,2-dichloroethene a higher boiling point than nonpolar trans-1, 2-dichloroethene.

Hydrogen Bonding

Hydrogen bonding is a special type of dipole-dipole forces that arise between molecules that have a hydrogen atom bound to a smaller sized, most electronegative atoms. These atoms are: Fluorine, Oxygen and Nitrogen. The bond formed between hydrogen and such an atom is highly polar. The partially positive (δ^+) H of one molecule is attracted to the partially negative (δ^-) lone pair on the F, O or N of the same or another molecule. As a result a hydrogen bond result. The atom sequence that leads to an H bond (*dotted line*) is indicated below. The following three examples illustrate the sequence.







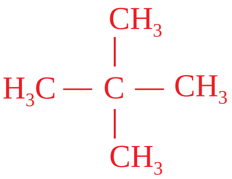
Hydrogen bonds hold water molecules in a rigid but open structure. When ice melts, some of the hydrogen bonds break. Water molecules move into the holes that are in the ice structures. The molecules are therefore closer together in liquid water than in ice. This means that liquid water at 0°C is denser than ice. Water is most unusual in this regard. When water on the surface of lakes and other areas freezes, the ice floats on the liquid water. If the solid were denser than the liquid as is true for nearly every other substance, the surface of the lake would freeze and sink until the entire lake was solid; aquatic plants and animals would be endangered.

Dispersion or London Forces

Intermolecular forces in which non-polar atoms or molecules interact by inducing dipoles in each other are known as dispersion or London Forces. These classes of intermolecular forces cause substances like CO_2, Cl_2, noble gases, etc, to condense and solidify. An attractive force must be acting between these non-polar molecules and atoms, or they would remain gaseous under any conditions. In fact, bond dipoles exert some weak attraction but the intermolecular forces are mainly responsible for the condensed state of non-polar substance. These forces are known as London forces or dispersion forces, named after Fritz London, the physicist who explained the quantum mechanical basis of the attractive forces.

Dispersion forces are very weak and are caused by a sudden shift of electron density to one side of the nucleus than the other. So the molecule has an instantaneous dipole. These instantaneous dipole will induce the neighbouring non-polar molecule. As a result, an induced-dipole is created. This process occurs throughout the sample and keeps the particles together. These dipoles are collectively known as dispersion forces or London forces. They are present between all particles (atoms, ions, and molecules.)

For substance with the same molar masses, the strength of the dispersion forces is often influenced by molecular geometry (*shape*). Shapes that allow more points of contact have more area over which electron clouds can be distorted, so stronger attractions result. This is probably the reason why n-pentane ($CH_3CH_2CH_2CH_2CH_3$) exhibits higher boiling point than its isomer 2,2-dimethyl propane.

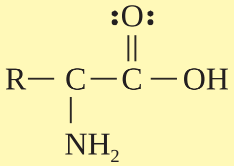


$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H_3C & - & C & - & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

Table 3. 1 Strength and polarity of intermolecular forces

Intermolecular force	Strength	Polarity
Hydrogen Bonding	The Strongest	Polar
Dipole-dipole Forces	Moderate	Polar
London Dispersion Forces	The Weakest	Non-polar

Exercise 3.11

1. In which of the following substances do hydrogen bonds occur? Explain with the help of diagrams.
   - a CH_4
   - b CH_3CH_2OH
   - c 
     $R-\underset{NH_2}{\underset{|}{C}}-\overset{:O:}{\overset{\|}{C}}-OH$
2. Identify the dominant intermolecular force that is present in each of the following substance and select the substance with the higher boiling point in each pair:
   - a CH_3OH or CH_3CH_2OH
   - b Hexane or cyclohexane
   - c $MgCl_2$ or PCl_3
   - d CH_3NH_2 or CH_3F
3. Which type of intermolecular force is dominant in the following substances?
   - a ICl
   - b H_2O
   - c F_2
   - d HBr
4. Compare intermolecular forces with that of intramolecular bonding.

3.4 METALLIC BONDING

At the end of this section, you should be able to:

- explain how metallic bond is formed;
- explain the properties of metals related to the concept of bonding; and
- carryout an activity to investigate the conductivity, malleability and ductility of some metals and non-metals (Al, Cu, Fe, Sn, Zn, S, C charcoal, C graphite and Si).

3.4.1 Formation of Metallic Bonding

Activity 3.18

Form a group and discuss the following:

1. Two characteristics that lead to an element being classified as a metal.
2. Type of bond existing in solid copper.
3. What is delocalisation of electrons?

4. Electron sea model.
5. Even though so much energy is required to form a metal cation with a 2+ charge, the alkaline earth metals form halides with general formula MX_2 rather than MX. Explain.

Share your ideas with the rest of the class.

In simple terms, metallic bonding is referred to as bonding in metal atoms. It is also defined as interaction between metal nuclei and the delocalized electrons. Delocalized electrons are also called as conduction electrons. Metals nuclei are the positive ions and so metallic bonding can be imagined as sea of electrons in which positive metal ions are embedded. Positive metal ions are called Kernels. Thus metallic bonding can be summarized as: The force of attraction which binds together the positive metal ions or Kernels with the electrons within its sphere of influence.

Is a metal made up of atoms or ions?

The strength of the metallic bond depends on the:

1. number of electrons in the delocalised 'sea' of electrons. (More delocalised electrons results in a stronger bond and a higher melting point.)
2. packing arrangement of the metal atoms.

   (The more closely packed the atoms are the stronger the bond is and the higher the melting point.)

3.4.2 Electron-Sea Model

The electron-sea model of metallic bonding proposes that all the metal atoms in the sample contribute their valence electrons to from "*sea*" of electrons, which is not localized for a particular atom. The metal ions (*the nuclei with their core electrons*) are submerged within this electron sea in an orderly array. See Figure 3.10.

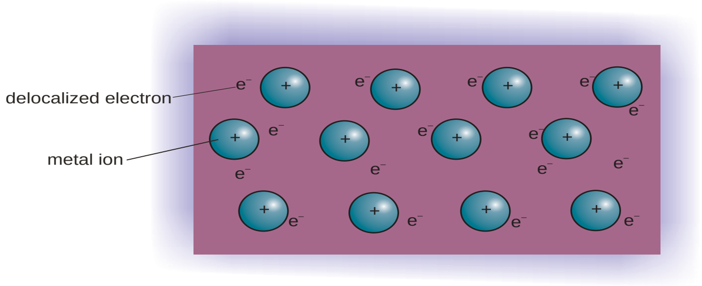


Figure 3.10 Schematic illustrations of electron-sea model for the electronic structure of metals.

In contrast to ionic bonding, the metal ions are not held in place as rigidly as in ionic solid. In contrast to covalent bonding, no particular pair of metal atoms is bonded through any localized pair of electrons. Rather, the valence electrons are shared among all the atoms in the substance, which is held together by the mutual attraction of the metal cations for the mobile, highly delocalized electrons. An electron-pair in a covalent resonance hybrid is delocalized over only a few atoms, but the extent of delocalization in metal is much greater. The bonding-electrons are free to move throughout the three dimensional structure.

3.4.3 Properties of Metals Related to the Concept of Bonding

Activity 3.19

Form a group and perform the following activity:

1. Take a piece of metal and a piece of wood of the same size.
2. Let these remain on a table so that both attain room temperature.
3. Place your left hand on the metal and right one on the wood.

What do you observe? Which hand feels colder? Why?

Discuss and share your findings with rest of the class..

The general properties of metals include malleability and ductility and most are strong and durable. They are good conductors of heat and electricity. Their strength indicates that the atoms are difficult to separate, but malleability and ductility suggest that the atoms are relatively easy to move in various directions. These properties suggest the nature of the metallic bonding between atoms.

Metallic bonds show typical metallic properties such as high electrical conductivity, lustre, and high heat conductivity. Metals are good conductors of electricity and heat because of their mobile electrons. They are strong and opaque in nature.

Most metals are malleable, which means that they can be hammered into thin sheets, and ductile, which means that they can be drawn into wires. These properties indicate that the atoms of the metallic lattice are capable of slipping with respect to one another. When a piece of metal is struck by a hammer, the metal ions move to a new lattice positions, sliding past each other through intervening electrons.

Most metals are solids with high melting and much higher boiling points; because the atoms of metals have strong attractive forces between them and much energy is required to overcome this force. For instance, the increase in melting point between the alkali metals [Group IA] and the alkaline earth metals [Group IIA] can be explained by the IIA metals having two valence electrons, available for metallic bonding, whereas the IA metals have only one. The greater attraction between the M^{2+} ions and twice the number of mobile electrons mean that higher temperatures are needed to melt such solid. The metals have a wide range of melting points, (from -39°C (mercury) to 3410°C (tungsten).

The properties of metals suggest that their atoms possess strong bonds, yet the ease of conduction of heat and electricity suggest that electrons can move freely in all directions in a metal. The general observations give rise to a picture of "positive ions in a sea of electrons" to describe metallic bonding.

Activity 3.20

Form a group and discuss the following questions:

1. Use the periodic table to arrange the following in order of increasing melting point K, Br_2, Mg and O_2. Explain the reason for the order you choose.
2. List four physical characteristics of a solid metal .
3. Briefly account for the following relative values:
    - a Lithium boils at 1317°C and melts at 179°C. The boiling point is about 1138°C higer than its melting point.
    - b The melting point of Li and Be are 180°C and 1287°C, respectively.
    - c The melting point of sodium is 89°C, where as that of potassium is 63°C.
4. For each of the following pairs, which element will have the greater metallic character:

    a Li or Be b Li or Na c Sn or Pb d B or Al?

Explain briefly. Share your ideas with the rest of the class.

Group Assignment

Form a group and do as directed:

1. You have been provided with aluminium, copper, iron, tin, zinc, charcoal, graphite and silicon. Complete the following table on your notebook. Perform experiment if required.

Sample	Conductivity	Malleability	Ductility
Aluminium			
Copper			
Iron			
Tin			
Zinc			
Charcoal			
Graphite			
Silicon			

2. Can you classify the samples as metal or non-metal?
3. Prepare another table and tabulate more properties of metals.

3.5 CHEMICAL BONDING THEORIES

At the end of this section, you should be able to:

- name two chemical bond theories;
- explain the valence bond theory;
- distinguish the Lewis model and the valence bond model;
- discuss the overlapping of orbitals in covalent bond formation;
- explain hybridization;
- show the process of hybridization involved in some covalent molecules;
- draw hybridization diagram for the formation of sp, sp^2, sp^3, sp^3d and sp^3d^2 hybrids;
- suggest the kind of hybrid orbitals on the basis of the electron structure of the central atom;
- predict the geometrical shapes of some simple molecules on the basis of hybridization and the nature of electron pairs.

- discuss the hybridization involved in compounds containing multiple bonds;
- explain bond length and bond strength;
- explain molecular orbital theory;
- describe molecular orbital-using atomic orbitals;
- describe bonding and anti bonding molecular orbitals;
- draw molecular orbital energy level diagrams for homonuclear diatomic molecules;
- write the electron configuration of simple molecules using the molecular orbital model;
- define bond order and determine the bond order of some simple molecules and molecule-ions;
- determine the stability of a molecule or an ion using its bond order; and predict magnetic properties of molecules.

The two modern chemical bonding theories which use quantum mechanics are the Valence Bond Theory (VBT) and the Molecular Orbital Theory (MOT).

3.5.1 Valence Bond Theory (VBT)

Lewis theory provides a simple, qualitative way to describe covalent bonding, and VSEPR theory allows us to carry the description further. Probable molecular shapes were predicted by VSEPR theory. Now consider a quantum mechanical approach to covalent bonding that confirms much of what is described through VSEPR theory, but which allows extending that description still further. The valence-bond approach is the most useful approach to answer questions like: what is a covalent bond? And how can we explain molecular shapes from the interaction of atomic orbitals?

The basic principle of valence bond theory is that a covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the nuclei, is occupied by a pair of electrons.

For instance, form an image in your mind of two hydrogen atoms approaching one another. The moment they get closer, their electron-charge clouds begin to combine into a whole. This intermingling is described as the overlap of the 1s orbitals of the two atoms. The overlap results in an increased electron charge-density in the region between the atomic nuclei. The increased density of negative charge serves to hold the positively-charged atomic nuclei together. In the valence bond (VB) method, a covalent bond is a region of high electron charge-density that results from the overlap of atomic orbitals between two atoms.

The strength of the bond between any two atoms generally depends on the extent of the overlap between the two orbitals. As the two atoms are brought more closely together, however, the repulsion of the atomic nuclei becomes more important than the electron-nucleus attraction and the bond become unstable. For each bond, then, there is a condition of optimal orbital overlap that leads to a maximum bond strength (bond energy) at a particular internuclear distance (*bond length*). The valence bond method attempt to find the best approximation to this condition for all the bonds in a molecule.

The bonding of two hydrogen atoms into a hydrogen molecule through the overlap of their 1s orbitals is pictured in Figure 3.11.

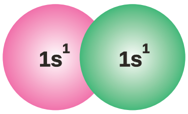


Figure 3.11 Atomic orbital overlap and bonding in H_2.

Note! The *s* orbital is spherical, but *p* and *d* orbitals have particular orientations - more electron density in one direction than in another - so a bond involving *p* or *d* orbitals will tend to be oriented in the direction that maximizes overlap.

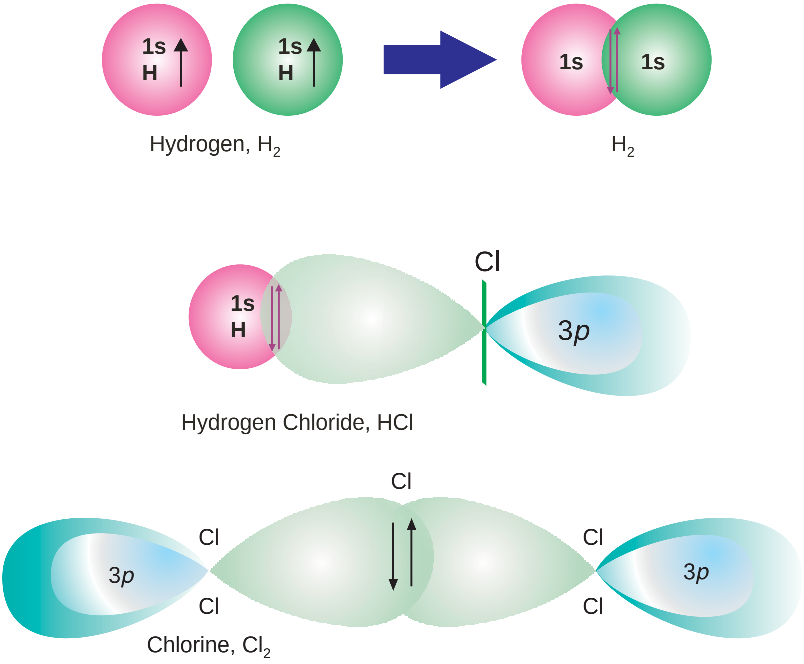


Figure 3.12 Oribital and spin pairing in three diatomic molecules.

In the HCl bond, for example, the 1*s* orbital of hydrogen overlaps the half-filled 3*p* orbital of Cl along the axis of that orbital. In Figure 3.11B any other direction would result in less overlap and, thus, a weaker bond. Similarly, in the Cl–Cl bond of Cl_2, the two 3*p* orbitals interact end-to-end, that is along the orbital axes, to attain maximum overlap (Figure 3.11C).

VSEPR theory predicts a tetrahedral bond angle (109.5°) in H_2S. However, if we take in to account the strong repulsions between the lone pairs of electrons on the S atom and the bond pairs, bonds are expected to be forced into a smaller angle. The measured bond angle in the H_2S molecule is 92.1°, suggesting that the valence bond method describes the covalent bonding in H_2S better than the VSEPR theory does (see Figure 3.12). There are not many cases, however, where the VB method produces superior results. A combination of VSEPR theory and the VB method are used in describing the shape of the molecules.

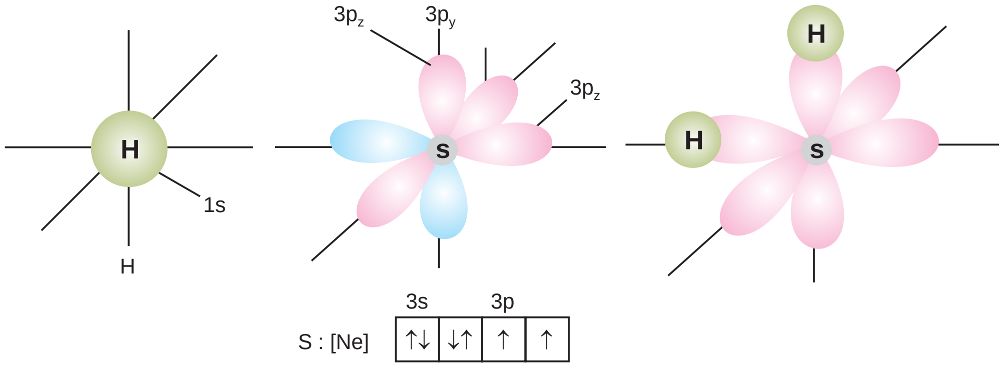


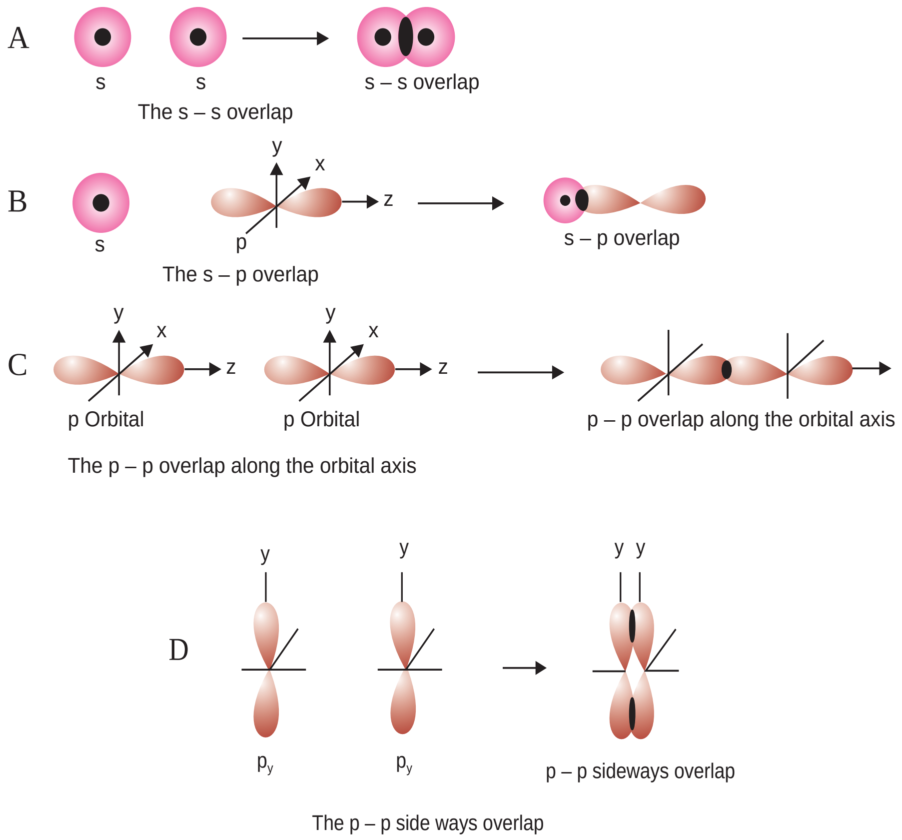
Figure 3.13 **Atomic oribitial overlap and bonding in H_2S.**

Overlap of Atomic Orbitals (Sigma and Pi Bonds)

To see the detailed makeup of covalent bonds, it is essential to focus on the mode by which orbitals overlap because orbital overlap is necessary for sharing of electrons and bond formation. Various type of atomic orbital overlap leads to covalent bond formation. Three simple basic ones are *s-s* , *s-p* and *p-p* shown in Figure 3.13.

1. *s-s* overlap in which half filled *s* orbitals overlap,
2. *s-p* overlap where half filled *s* orbital of one atom overlaps with one of the *p* orbital having one electron only and

3. *p-p* overlap in which two half filled *p* orbitals overlap.



The s – s overlap

The s – p overlap

The p – p overlap along the orbital axis

The p – p side ways overlap

Figure 3.14 Atomic orbital overlap.
(*A*) s-s overlap, (B) s-p overlap, (C) p-p overlap along the orbital axis and (D) p-p sideways overlap.

Because of the directional nature of *p* orbital, the overlap may take place in two ways: (i) the half filled p orbitals along the line joining the two nuclei. This is called as head on, end-to-end, end on or linear overlap and (ii) the half filled *p* orbitals overlap along the line perpendicular to the nuclear axis. This overlapping of p orbitals is parallel to each other, hence is called lateral or sideways overlapping. These two modes give rise to the two types of covalent bonds, namely, sigma (σ) and pi (π) bond respectively. Valence bond theory is used to describe the two types here, but they are essential features of molecular orbital theory as well. *s* - *s* and *s* - *p* will always overlap along the nuclear axis, hence results only in sigma bonds.

Sigma bond has its highest electron density along the bond axis (an imaginary line joining the nuclei) in between the bonded nuclei. All single bonds have their electron density concentrated along the bond axis, and thus are sigma bonds.

A side - to - side or parallel overlap forms another type of covalent bond called a pi (π) bond. It has two regions of electron density. One above and one below the sigma bond axis. One π-bond holds two electrons that occupy both regions of the bond. A double-bond always consists of one σ and one π bond. The double-bond increases electron density between the nuclei. A triple bond consists of one σ and two π bonds.

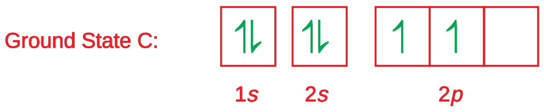
Now it can be seen clearly why a double and triple bonds were considered as one electron set in the discussion of VSEPR. The reason is that each electron pair occupies a distinct orbital, a specific region of electron density, so repulsions are reduced.

The extent of overlap influences bond strength, however, many factors, such as lone - pair repulsions, bond polarities, and other electrostatic contributions affect overlap and the relative strength of σ and π bonds between other pairs of atoms. Thus as a rough approximation, a double bond is about twice as strong as a single bond, and a triple bond is about three times as strong.

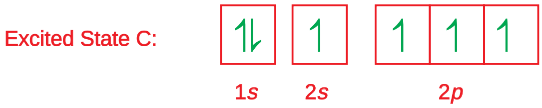
Hybridization of Orbitals

Valence bond theory employs the concept of hybridization. It is the overlap or blending of *s*, *p* and *d* orbitals to explain bond formation.

In applying the valence bond method to the ground state electron configuration of carbon you can assume that the filled 1*s* orbital will not be involved in the bonding and focus your attention on the valence-shell orbitals.



From its ground state configuration, two unpaired electrons in the 2*p* subshell are observed. One can predict the simplest hydrocarbon molecule to be CH_2, by overlapping the two unpaired electrons from two H atoms with the two unpaired electrons of carbon. However, you might question the existence of this molecule because it does not follow the octet rule. In fact, experiment shows that CH_2 is not a stable molecule. The simplest stable hydrocarbon is methane, CH_4. To account for this, you need an orbital diagram that shows four unpaired electrons in the valence shell of carbon, requiring four bonds (and therefore four atoms of hydrogen). To get such a diagram imagine that one of the 2*s* electrons is promoted to the empty 2*p* orbital. To excite the 2*s* electron to a higher energy sublevel, energy must be absorbed. The resulting electron configuration is that of an excited state having energy greater than the configuration in the ground state.



Valence bond theory proposes that the one 2*s* and all three 2*p* orbitals of the carbon atom 'mix' to produce four new orbitals that are equivalent to each other in energy and in shape and pointing in different directions with equal H–C–H bond angles. This blending is called hybridization and the resultant orbital as hybrid orbitals. It is a hypothetical process (not an observed one) that can be carried out as a quantum mechanical calculation. The symbols used for hybrid orbitals identify the kinds and numbers of atomic orbitals used to form the hybrids.

In hybridization scheme, *the number of new hybrid orbitals is equal to the total number of atomic orbitals that are combined.*

Hybridization provides a useful and convenient method of predicting the shapes of molecules. It must be noted that though it is valuable in predicting and describing the shape, it does not explain the reason for the shape.

Exercise 3.12

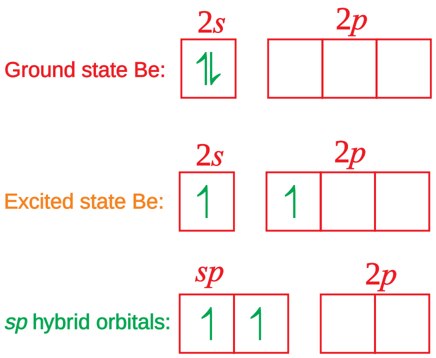
1. How do carbon and silicon differ with regard to the types of orbitals available for hybridization? Explain
2. Are these statements true or false? Correct any that is false.
   - a Two σ bonds comprise a double bond.
   - b A triple-bond consists of one π bond and two σ bonds.
   - c Bonds formed from atomic *s* orbitals are always σ bonds.
   - d A π-bond consists of two pairs of electrons
   - e End-to-end overlap results in a bond with electron density above and below the bond axis.

sp hybrid orbitals

When two electron sets surround the central atom, you observe a linear molecular shape. VB theory explains this by proposing that mixing two non-equivalent orbitals of a central atom one s and one *p*, gives rise to two equivalent sp hybrid orbitals that lie 180° apart. Combination (mixing) of one s and one p orbital is called *sp* hybridization and the resultant orbitals are called *sp* hybrid orbitals.

For instance, the beryllium atom has two electrons and four orbitals in its valence shell. In the triatomic molecule $BeCl_2$, which is present in gaseous $BeCl_2$ at high temperatures, the 2*s* and one of the 2*p* orbitals of the Be atom are hybridized into *sp* hybrid orbitals. The remaining two 2*p* orbitals are left unhybridized and unoccupied in the orbital diagram.

Since there are no unpaired electrons this atom cannot form any covalent bonds. It follows that in $BeCl_2$, the Be atom is not in the ground state but it is in the excited state, with sufficient extra energy to unpair a 2*s* electron.



As shown in Figure 3.15 the two *sp* hybrid orbitals are directed along a straight line, 180° apart. It is predicted that the $BeCl_2$ molecule should be linear, and this

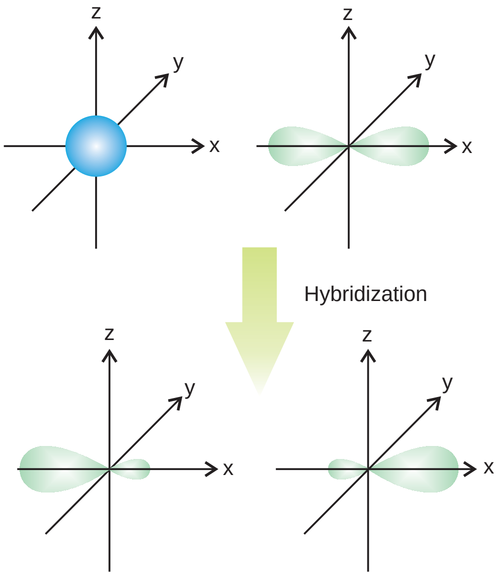


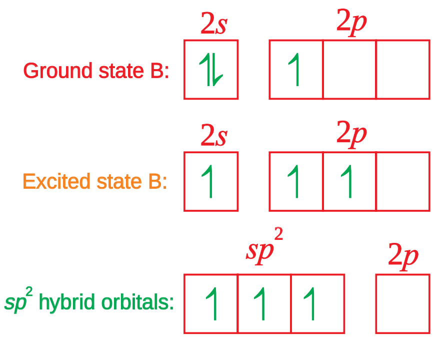
Figure 3. 15 The *sp*-hybridization scheme illustrated.

prediction is confirmed by experimental evidence. Most examples of *sp* hybridization are found in organic molecules, especially those with triple bonds.

sp^2 hybrid orbitals

Now turn your attention to boron, a Group IIIA element. The boron atom has four orbitals but only three electrons in its valence shell. In most boron compounds the hybridization scheme combines one 2*s* and two 2*p* orbitals into three sp^2 hybrid orbitals. Using orbital diagrams to represent this hybridization, we have

sp^2 hybrization for B



The atom in its ground state has only one unpaired electron, so that it can form only one covalent bond, but in the excited state there are three unpaired electrons, hence three bonds can be formed.

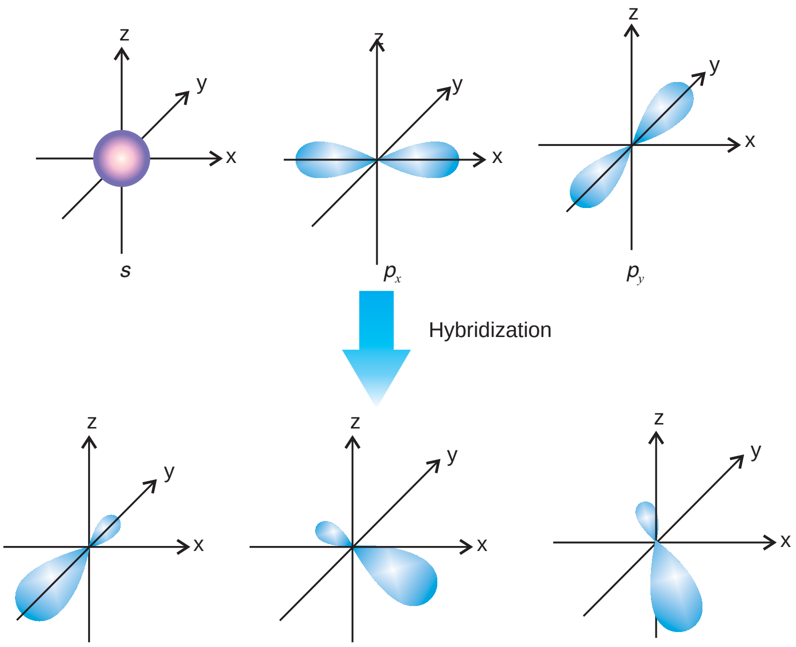


Figure 3.16 The sp² hybridization scheme illustrated.

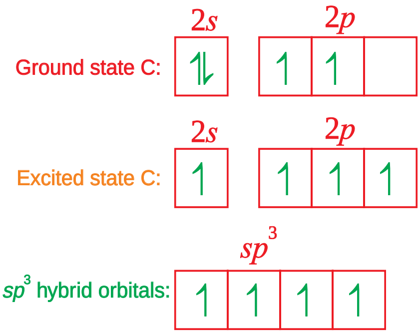
As shown in Figure 3.15 the *sp*^{2} hybrid orbitals are distributed geometrically within a plane at 120° angles. The valence bond method predicts that BCl_3 is a trigonal planar molecule with 120° Cl–B–Cl bond angle. This indeed is what is observed experimentally.

By far the most common examples of *sp*^{2} hybridization are found in organic molecules with double bonds.

sp^3 hybridization

Carbon, the central atom in a molecule of methane CH_4 has only two unpaired electrons in the ground state. The two electrons in the 2*p* level are not paired, *i.e.*, put into the same box, in accordance with Hund's rule. Carbon in its excited state can form four bonds. The one 2*s* and three 2*p*-orbitals of carbon are mixed to produce four new orbitals that are equivalent to each other in energy and in shape, but pointing in different directions, as shown in Figure 3.17.

sp^3 hybridization for carbon



The four *sp*^{3} hybrid orbitals point to the corners of a regular tetrahedron, and make a bond angle of 109.50° in CH_4 (Figure 3.17).

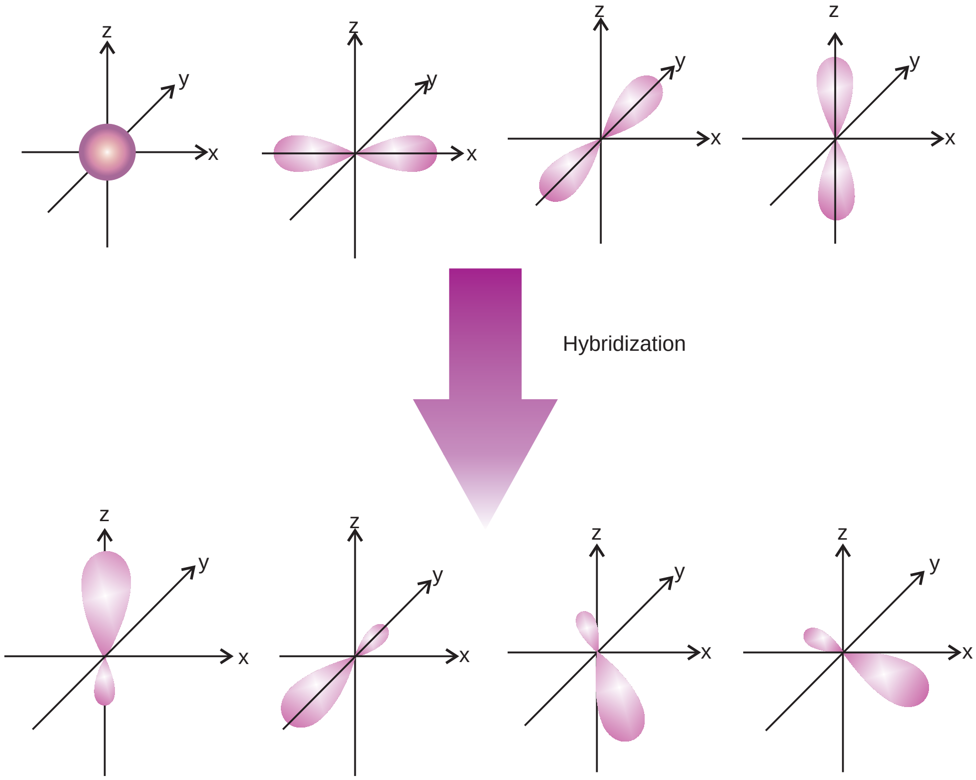


Figure 3.17 **The *sp*^{3} hybridization.**

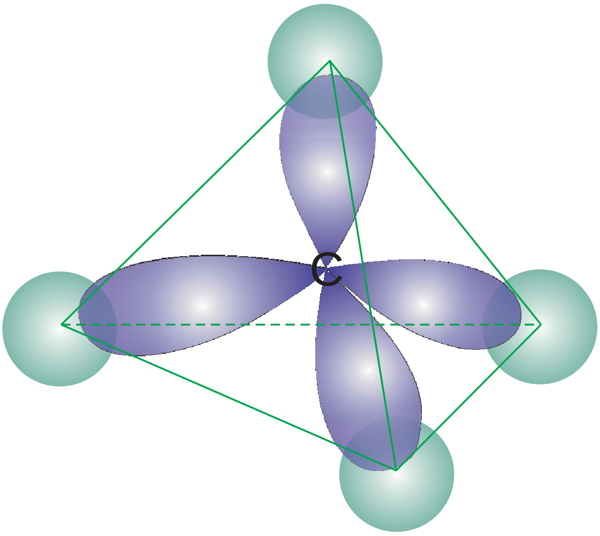
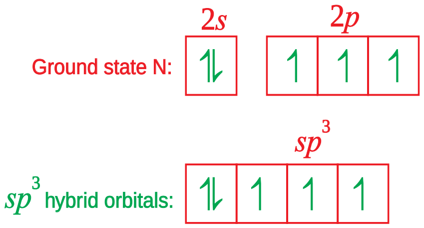


Figure 3.18 ***sp*^{3} Hybrid orbitals and bonding in methane scheme illustrated.**

We might also expect to use sp^3 hybridization not only for structures of the type AX_4 type (as in CH_4), but also for AX_3E type (as in NH_3) and AX_2E_2 type (as in H_2O). Nitrogen has three unpaired electrons in its ground state, sufficient to form three bonds; so it is not necessary to excite the atom. sp^3 hybridization of the central atom N in NH_3



accounts for the formation of three N–H bonds and a lone-pair of electrons on the N atom (Figure 3.19). The predicted H–N–H bond angles of 109.5° are close to the experimentally observed angles of 107°.

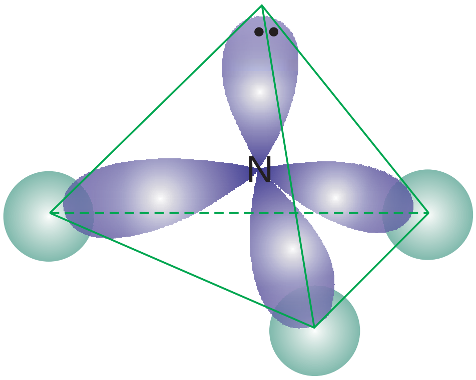
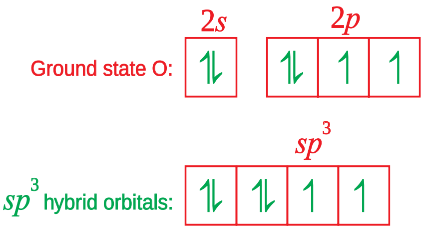


Figure 3.19 ***sp*³ hybrid orbitals and bonding in NH₃.**

A similar scheme for H_2O accounts for the formation of two O–H bonds and two lone-pairs of electrons on the oxygen atom.

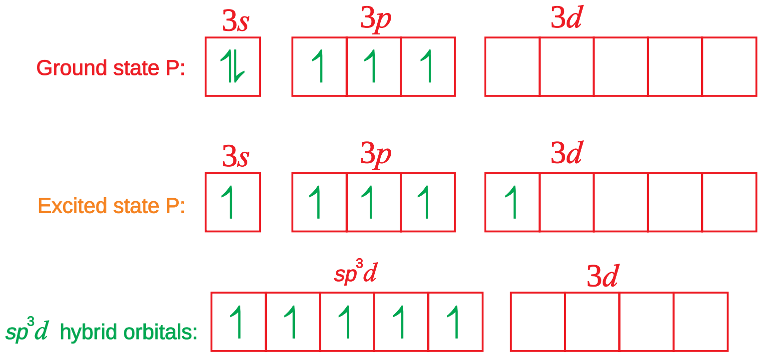


The predicted H–O–H bond angle of 109.5° is also reasonably close to the observed angle of 104.5°. As in our discussion of the VSEPR theory, we can explain somewhat smaller than tetrahedral bond angles in NH_3 and H_2O in terms of repulsions involving lone-pair electrons.

sp^3d hybridization

A maximum of eight valence electrons can be accommodated by any hybridization scheme involving only s and *p* orbitals. Hybridization schemes for structures involving expanded octets must include additional orbitals and these extra orbitals can come from a *d*-subshell.

For example, we need five hybrid orbitals to describe bonding in PCl_5. In a gaseous molecule of phosphorus pentachloride, PCl_5, the central atom phosphorus has only three unpaired electrons in its ground state. Electrons must be unpaired to provide the correct number of unpaired electrons for bond formation.



Five orbitals are being used and sp^3d hybridization occurs, giving a trigonal bipyramidal structure. The sp^3d hybrid orbital and their trigonal bipyramidal structure is shown in Figure 3.20.

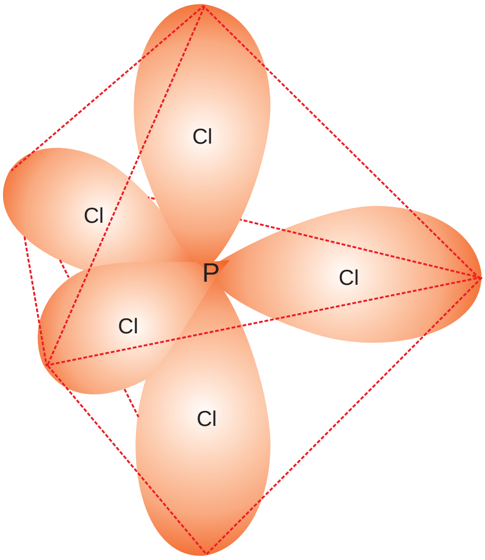


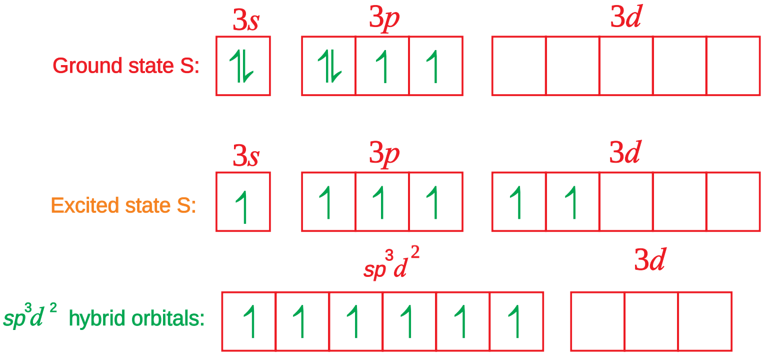
Figure 3.20 The sp^3d hybrid orbitals in the molecule of PCl_5.

Like other hybrid orbitals we have considered, the five *sp*^{3}*d* hybrid orbitals are arranged in a symmetrical fashion, but unlike the other case, the five *sp*^{3}*d* orbitals are not all equivalent. Three of the orbitals are directed in the plane of the central atom at 120° angles with one another; the remaining two are perpendicular to the plane of the other three. The three positions in the central plane are called the equatorial positions and the two positions perpendicular to the plane are called axial positions.

Hybridization may take place only between orbitals of roughly the same energy. It follows that it is not possible to hybridize the 2*s* or 2*p* levels with the 3*s*, or the 3*s* or 3*p* level with the 4*s*. The *d* levels are intermediate in energy, and may in certain circumstance be used with the energy levels either below or above, that is 3*s* with 3*d*, and 3*d* with 4*s* are both possible.

sp^3*d*^{2} Hybridization

Another structure featuring an expanded octet is SF_6. Here, six hybrid orbitals are required in order to describe bonding. These are obtained through the hybridization scheme *sp*^{3}*d*^{2}, represented by the orbital diagrams.



The *sp*^{3}*d*^{2} hybrid orbitals and their octahedral orientation are shown in Figure 3.21.

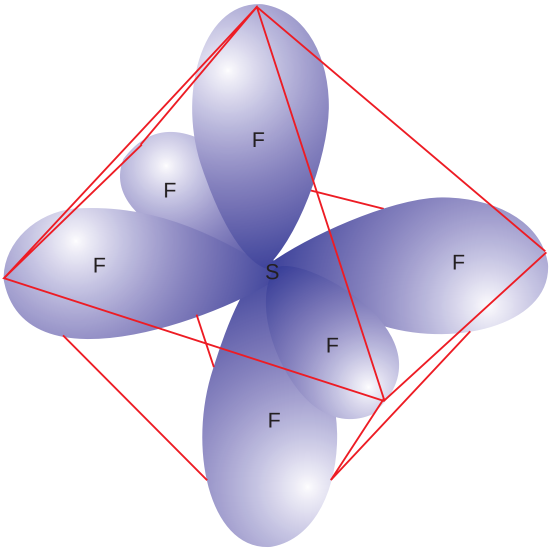


Figure 3.21 The sp^{3}d^2 hybrid orbitals SF_6.

In hybridization schemes, one hybrid orbital is produced for every single atomic orbital involved. In a molecule, each of the hybrid orbitals of the central atom acquires an electron pair, either a bond-pair or a lone-pair. And the hybrid orbitals have the same orientation as the electron-set arrangement predicted by VSEPR theory.

When one describes the probable hybridization scheme for a structure, he/she must choose a scheme that conforms to experimental evidence. This can be done by mixing the VSEPR and valence bond approaches. The procedure is outlined in the following four steps and illustrated in Example 3.4.

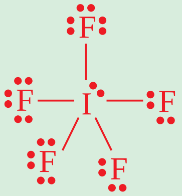
1. Write a reasonable Lewis structure for the species
2. Use VSEPR theory to predict the electron-set arrangement of the central atom
3. Select the hybridization scheme that correspond to the VSEPR prediction
4. Describe the orbital overlap

Example 3.3

Describe a hybridization scheme for the central atom of iodine pentafluoride, IF_5.

Solution:

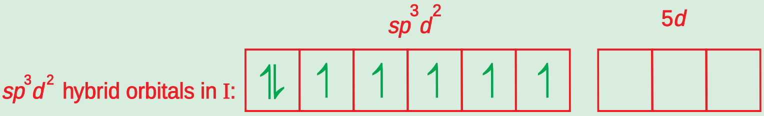
a The reasonable Lewis structure for IF_5 is



b VSEPR predicts an octahedral electron-set arrangement for six electron pairs (AX_6 type)

c The hybridization scheme corresponding to octahedral electron arrangement is sp^3d^2

d The six sp^3d^2 hybrid orbitals are directed to the corners of an octahedron, but one of the orbitals is occupied by a lone pair of electrons (*shown in red below*).

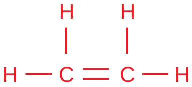


The resulting molecular shape is that of a square pyramid with bond angles of approximately 90°.

Exercise 3.13

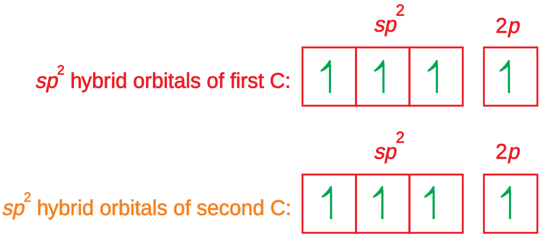
1. Name the three types of hybrid orbitals that may be formed by an atom with only *s* and *p* orbitals in its valence shell. Draw the shapes of the hybrid orbitals so produced.
2. Describe a hybridization scheme for the central atom and molecular geometry of the triiodide ion, I_3^-.

The use of VSEPR theory to predict geometric structures of molecules and polyatomic ions with double and triple covalent bonds has already been described.. When you combine this knowledge with the valence bond method, you gain additional insight. For example, the Lewis structure of ethene (*ethylene*) is depicted as



$$\mathrm{H}-\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}=\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}-\mathrm{H}$$

With VSEPR theory you predicted that the electron set geometry around each carbon atom is trigonal planar (AX_3 type). This corresponds to H–C–H bond angles of 120°. To account for these bond angles in the valence bond method, you assume that the 2*s* and two of the 2*p* orbitals of the valence shell combine to produce sp^2 hybridization of the two carbon atoms.



All the C–H bonds in C_2H_4 are formed by the overlap of sp^2 hybrid orbitals of the C atoms with 1*s* orbitals of the H atom, with these orbitals directed along hypothetical lines joining the nuclei of the bonded atoms. A double covalent bond consists of one σ and one π bond. The features of a double bond described here are illustrated in Figure 3.22.

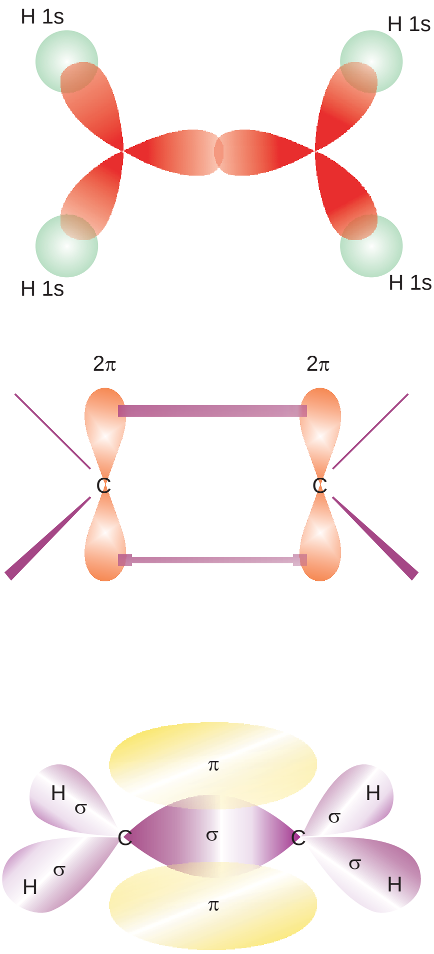


Figure 3.22 Bonding in ethylene, C_2H_4.

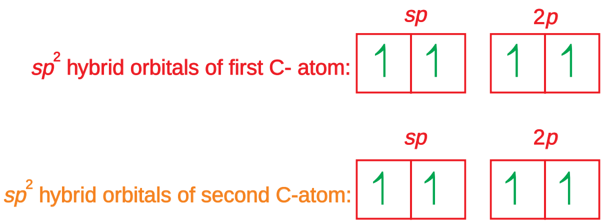
VSEPR theory describes $H_2C = CH_2$ as consisting of two planar CH_2 groups, each with a 120° H–C–H bond angle. But it does not tell us how the two groups are oriented with respect to one another. Are they both in the same plane? Is one perpendicular to the other? The valence bond description of a double-bond gives the answer. The maximum sidewise overlap between the unhybridized 2*p* orbitals to form a π bond occurs when both CH_2 groups lie in the same plane. Ethene is a planar molecule. If one CH_2 group is twisted out of the plane of the other, the extent of overlap of the 2*p* orbitals is reduced, the π bond is weakened, and the molecule becomes less stable.

Aside from the restriction in rotation about a double bond just described, electron pairs in π bonds do not fix the positions of bonded atoms to one another. These positions are established by the σ bonds, the so-called sigma-bond frame-work, and there is only one σ bond framework because all the electrons in a multiple covalent bond constitute a single electron set.

We can describe a triple covalent bond in a manner similar to that just used for a double bond. Consider the Ethyne (acetylene) molecule, C_2H_2. Its Lewis structure is

$$H - C \equiv C - H$$

The molecule is linear, with 180° H–C–C bond angles, as predicted by VSEPR theory and confirmed by experiment. To account for these bond angles with the valence bond method, we assume *sp* hybridization of the valence shell orbitals of the two C atoms.



In the C ≡ C bond in C_2H_2, as in all triple bonds, one bond is a σ-bond and two are π- bonds.

The bonding scheme in acetylene is illustrated in Figure 3.23.

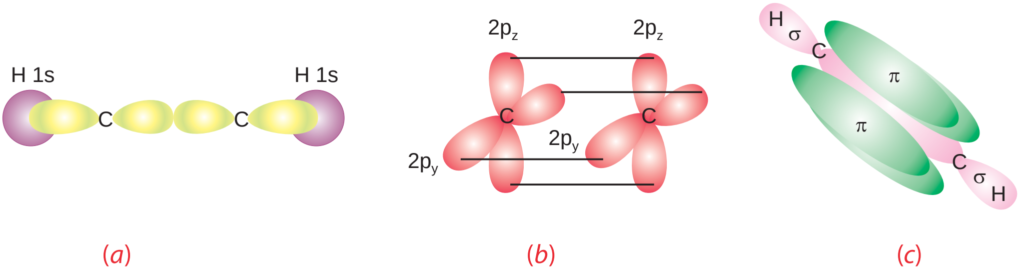


Figure 3.23 Bonding in acetylene, C_2H_2.

Exercise 3.14

1. Describe a hybridization scheme for the central atom S and the molecule geometry of

   a SO_3 and b SO_2

2. Describe a hybridization scheme for the central atom and the molecular geometry of CO_2.
3. Discuss the bonding in nitrate ion, predict the ideal bond angles, bond length, shape of the ion, the number of sigma and pi bonds.

3.5.2 Molecular Orbital Theory (MOT)

Molecular orbital theory is a method of accounting for covalent bonds that depends on quantum theory and mathematical principles. This theory is based on the fact that electrons are not the substantive little dots as we portray in Lewis structures. We can speak only about energy levels/spatial probabilities when reckoning with them. We do this reckoning by thinking of quantized electron distribution as atomic orbitals (AOs) [*spdf*].

Combination of Atomic Orbitals

Atomic orbitals are capable of combining or overlapping, to produce new electron distributions called molecular orbitals (MOs) – one MO for every AO. The quantum mechanical treatment of electrons in atoms as matter waves yields atomic orbitals (AOs). A similar treatment applied to electrons in molecules yields molecular orbitals (MOs), which are mathematical descriptions of regions of high electron charge density in a molecule. It is easy to understand molecular orbital theory in principle; we seek an arrangement of appropriately placed atomic nuclei and electrons to produce an energetically favourable, stable molecule. The difficulty comes in practice, in trying to construct a wave equation for a system of several particles. The usual approach is to write approximate wave equations by relating them to atomic orbitals.

Bonding and Anti-Bonding Molecular Orbitals

Bonding molecular orbitals have a region of high electron density between the nuclei. Anti-bonding molecular orbitals have region of zero electron density (a node) between the nuclei. Typical results are like those shown for H_2 molecule in Figure 3.23. In place of atomic orbitals of the separated atoms, the molecular orbitals for the united atoms are obtained, and these are of two types. One type, a bonding molecular orbital, places a high electron charge density in between the two nuclei and the other type, an anti-bonding molecular orbital, places a high electron charge density away from the region between the two nuclei. Electrons in bonding orbitals contribute to bond formation and electrons in anti-bonding orbitals detract from bond formation.

When two atomic orbitals overlap end-to-end, they form two sigma-molecular orbitals (MOs). Consider the H_2 molecule, which has two H atoms and therefore two 1*s* AOs. The two 1*s* atomic orbitals combine (see Figure 3.23) to produce two σ MOs, which differ in energy and location. One of the σ MOs is a bonding orbital, denoted σ_{1s}, the other is an anti-bonding orbital denoted σ^*_{1s}.

The relative energy levels of these two MOs are different. The σ_{1s} MO has a lower energy than the original 1*s* AOs, while the σ^*_{1s} MO has a higher energy.

Electron Configuration of Diatomic Molecules

After applying two principles of filling orbitals

- The *aufbau* principle and
- The Pauli exclusion principle

we can predict that both electrons in H_2 will go into the lower energy orbital denoted by $(\sigma_{1s})^2$. A molecular-orbital diagram shows the relative energy and number of electrons in each MO, as well as the atomic orbitals from which they form. Figure 3.24 is the molecular orbital diagram for H_2.

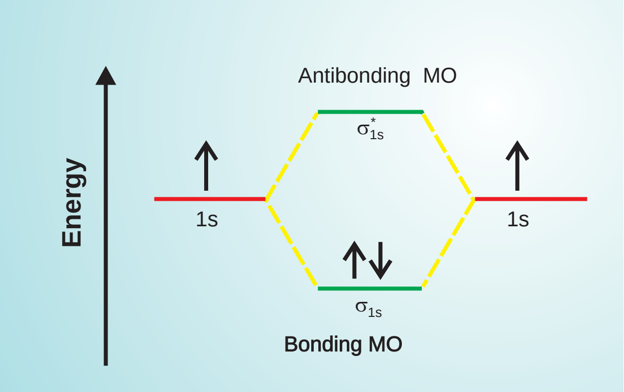


Figure 3.24 Molecular orbital diagram and bonding in the H_2 molecule.

There are no more electrons in H_2 so the σ^*_{1s} orbital remains empty in the ground state.

Note! The number of molecular orbitals formed must equal the number of atomic orbitals available for combination. Unfilled molecular orbitals are considered to be there, even when there are no electrons in them.

Exercise 3.15

Draw a molecular orbital energy diagrams for

a C_2^- b C_2 c C_2^+

The order of energy of molecular orbitals has been determined mainly from spectroscopic data.

a In simple homonuclear diatomic molecules (total electrons = 14 or less) the order is:

$$\sigma_{1s}\sigma_{1s}^*\sigma_{2s}\sigma_{2s}^*\left(\pi_{2p_y}=\pi_{2p_z}\right)\sigma_{2p_x}\left(\pi_{2p_y}^*=\pi_{2p_z}^*\right)\sigma_{2p_x}^*$$

b For simple homonuclear diatomic molecules (total electrons greater than 14) the $\left(\pi_{2p_y}=\pi_{2p_z}\right)$ comes after σ_{2p_x} and the order is:

$$\sigma_{1s}\ \sigma_{1s}^*\ \sigma_{2s}\ \sigma_{2s}^*\ \sigma_{2p_x}\ (\pi_{2p_y}=\pi_{2p_z})\ (\pi_{2p_y}^*=\pi_{2p_z}^*)\ \sigma_{2p_x}^*.$$

Note that the $2p_y$ atomic orbital give π bonding and π antibonding (π^*) MOs of the same energy as those produced from $2p_z$ orbitals. The π_{2p_y} and π_{2p_z} orbitals are said to be double degenerate, and similarly $\pi_{2p_y}^*$ and $\pi_{2p_z}^*$ are double degenerate. A similar arrangement of MOs exists from σ_{3s} to $\sigma_{3p_x}^*$, but the energies are known with less certainty.

The Aufbau principle is used to derive the electronic structure of some simple diatomic molcules or molecule ions. The total number of electrons from the two atoms which make the molecule are filled into molecular orbitals. The MOs of lowest energy are filled first, each MO holds two electrons of opposite spins and when orbitals are degenerate, Hund's rule applies and electrons are not paired.

Example 3.4

Use the molecular orbital theory to derive the electron configuration of

a H_2^+ b Li_2 c He_2^+ d O_2. Which of these molecules or molecules ions exist?

Solution:

a H_2^+ molecule ion. This may be considered as a combination of H atom and a H^+ ion, giving one electron to be accommodated in a MO;

b Li_2 molecule. Each Li atom has two electrons in its inner shell, and one in its outer shell, making a total of six electrons arranged:

$(\sigma_{1s})^2\ (\sigma^*_{1s})^2\ (\sigma_{2s})^2$

c He_2^+ Molecule ion. If this is considered as a He atom and a He^+ ion there are three electrons, which are arranged. The filled bonding orbital gives stabilization whilst the half-filled gives destabilization. Overall, there is some stabilization, so the helium molecule ion should exist, and it has been observed spectroscopically.

$(\sigma_{1s})^2\ (\sigma^*_{1s})^2$

d O_2 molecule. Each oxygen has eight electrons, making a total of sixteen for the molecule. These are arranged:

$$(\sigma_{1s})^2\ (\sigma^*_{1s})^2\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\sigma_{2px})^2 \left\{\begin{matrix}(\pi_2 p_y)^2 \\ (\pi_2 p_z)^2\end{matrix}\right. \left\{\begin{matrix}(\pi^*_{2\,p_y})^1 \\ (\pi^*_2 p_z)^1\end{matrix}\right.$$

The anti bonding ($\pi^*_{2p_y}$) and ($\pi^*_{2p_z}$) orbitals are singly occupied in accordance with Hund's rule. As in previous examples, the inner shell does not participate in bonding and the bonding and antibonding 2*s* orbitals cancel each other. A σ bond results form the filling of $(\sigma_{2px})^2$. Two half π bonds arise form π_{2p_z} and π_{2p_y} bonding and

antibonding. Therefore, $1\sigma + \frac{1}{2}\pi + \frac{1}{2}\pi = 2$ bonds are formed.

Exercise 3.16

Use the molecular orbital theory and derive the electron configuration of the following molecules. Identify those which exist and do not exist.

a He_2 b Be_2 c B_2 d C_2 e N_2

Bond Order

The term bond order is used to indicate whether a covalent bond is single (bond order = 1), double (bond order = 2) or triple (bond order = 3). For example, in a molecular orbital treatment of oxygen, a sigma bond results from the filling of $(\sigma_{2px})^2$. Since $(\pi^*_{2py})^1$ is half-filled therefore cancels half the effect of $(\pi_{2py})^2$, half a pi bond results. Similarly another half pi bond arise from π_{2pz} and π^*_{2pz}, giving a total of $1\sigma + \frac{1}{2}\pi + \frac{1}{2}\pi = 2$. The bond order is said to be 2, and it can be calculated in the above manner, or by calculating the number of electrons occupying bonding orbitals minus the number of electrons in antibonding orbitals, all divided by two.

$$\text{Bond order} = \frac{1}{2}\left[\begin{pmatrix}\text{Number of } e^- \text{ in} \\ \text{bonding MOs}\end{pmatrix} - \begin{pmatrix}\text{Number of } e^- \text{ in} \\ \text{antibonding MOs}\end{pmatrix}\right]$$

Activity 3.21

Form a group and use the MO theory to predict the bond order and the number of unpaired electrons in O_2^{2-}, O_2^-, O_2^+, NO and CO.

Share your findings with the rest of the class.

Magnetic Properties

A species with unpaired electrons exhibits paramagnetic property. The species is attracted by an external magnetic field. A species in which all the electrons are paired, exhibits diamagnetism. Such species are not attracted (and, in fact, are slightly repelled) by a magnetic field.

The antibonding π^*_{2py} and π^*_{2pz} orbitals for O_2 are singly occupied in accordance with Hund's rule. Unpaired electrons give rise to paramagnetsim. Since there are two unpaired electrons with parallel spins, this explains why oxygen is paramagnetic. This was the first success of the MO theory in successfully predicting the paramagnetisim of O_2, a fact not even thought of with VB representation of the oxygen molecule (O == O).

Exercise 3.17

1. What is the bond order for CN^-, CN and CN^+?
2. Which homonuclear diatomic molecules of the second period elements, besides O_2, should be paramagnetic?

3.6 TYPES OF CRYSTALS

At the end of this section, you should be able to:

- define a crystal;
- name the four types of crystalline solids and give examples;
- mention the types of attractive forces that exist within each type of crystalline solids;
- describe the properties of each type of crystalline solids; and
- build a model of sodium chloride crystal structure.

A crystal is a piece of a solid substance that has plane surface, sharp edges, and a regular geometric shape. The fundamental units-atoms, ions or molecules are assembled in a regular, repeating manner extending in three dimensions throughout the crystal. An essential feature of a crystal is that its entire structure can be figured from a tiny portion of it. Some solids, like glass, lack this long-range order and are said to be amorphous. The structural units of an amorphous solid, whether they are atoms, molecules or ions occur at random positions. As in liquids, there is no ordered pattern to the arrangement of an amorphous solid.

A structural unit of a crystalline solid has a characteristic repetitive pattern. The crystal types and their basic units are (i) ionic (electrostatic attraction of ions), (ii) Molecular (electrostatic attraction of dipoles in molecules) (a) Polar (dipole-dipole and H-bonding) and (b) Non-polar (London forces) (iii) Network (covalently bonded atoms); and (iv) metallic (positive nuclei in electron sea).

There are four important classes of crystalline solids.

Ionic Crystals

The fundamental units of an ionic solids are positive and negative ions. As a result, the inter-particle forces (ionic bonds) are much stronger than the van der Waals forces in molecular solids. To maximize attractions, cations are surrounded by as many anions as possible, and vice versa.

The properties of ionic solids are direct consequences of the strong inter-ionic forces, which create a high lattice energy. Crystalline ionic solids are usually, brittle, and non-conductors of electricity, although molten crystals may be good conductors. They usually have high melting points. Some of the more familiar ionic solids are table salt ($NaCl$), saltpeter (KNO_3), washing soda ($Na_2CO_3.10H_2O$), and black board chalk ($CaCO_3$).

Group Assignment

With the help of balls and sticks of any material or any other modelling material build the model of crystal sodium chloride. [Hint-Take help of Figure 3.25]

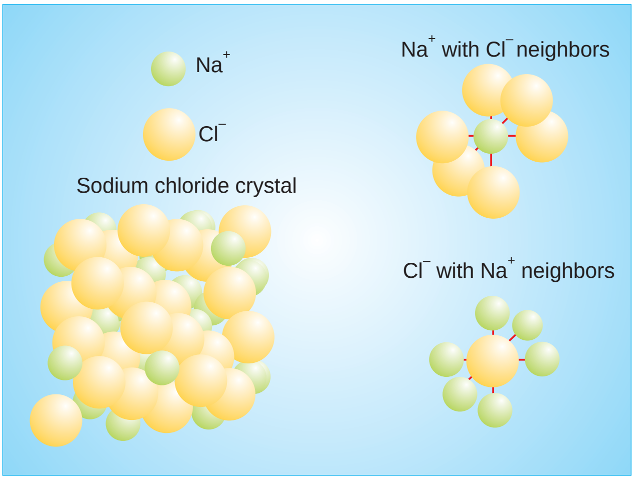


Figure: 3. 25 Crystal model of sodium chloride.

Molecular Crystals

Various combinations of dipole-dipole, dispersion and hydrogen-bonding forces are operative in molecular solids, which accounts for their wide range of physical properties. Dispersion forces are the principal forces acting in non-polar substances, so melting points generally increase with molar mass. Among polar molecules, dipole-dipole forces and where ever possible, hydrogen-bonding dominate. Nevertheless, intermolecular forces are still relatively weak, so the melting points are much lower than ionic, metallic and network covalent solids.

The fundamental unit of a molecular solid is the molecule. Such solids are common among organic compounds and simple inorganic compounds. Molecular crystals are usually transparent, brittle, and break easily when stressed. They are usually non conductors of heat and electricity and usually have low melting points. Familiar molecular crystalline solids include sugar, dry ice (solid carbon dioxide), glucose and aspirin.

Covalent Network Crystals

In this type of crystalline solids, separate particles are not present. Instead, strong covalent bonds link the atoms together throughout the network of covalent solid. As a consequence of the strong bonding, all these substances have extremely high melting and boiling points, but their conductivity and hardness depend on the nature of their bonding. The two common crystalline forms of elemental carbon are examples of network covalent solids. Although graphite and diamond have the same composition, their properties are strikingly different, graphite occurs as stacked flat sheets of hexagonal carbon rings with a strong sigma-bond framework and delocalized pi-electrons over the entire sheet. These mobile electrons allow graphite to conduct electricity. Common impurities, such as O_2 makes graphite soft. In diamond, each carbon atom is bonded to four other carbon atoms tetrahedrally in a giant structure. The carbons are joined by single bonds. Strong single bonds throughout the crystal make diamond among the hardest substance known. Because of its localized bonding electrons, diamond (like most network covalent solids) is unable to conduct electricity. The most important network covalent solids are the silicates. In a covalent network solid, the whole crystal is one giant molecule. The fundamental units are atoms covalently bonded to their neighbours. These crystals are usually hard, non conductors of heat and electricity, and have high melting points. Examples of covalent network solids include quartz (SiO_2) and diamond.

Metallic Crystals

The strong metallic bonding forces hold individual atoms together in metallic solids. The properties of metals, such as high electrical and thermal conductivity, luster and malleability result from the presence of delocalized electrons, the essential feature of metallic bonding (introduced in Section 3.4). Metals have a wide range of melting points and hardness, which are related to the packing efficiency of the crystal structure and the number of valence electrons available for bonding. For example, Group IIA metals are harder and higher melting than Group IA metals, because the IIA metals have closer packed structures and twice as many delocalized valence electrons.The fundamental units of pure metallic solids are identical metal atoms. Metallic crystals are opaque with reflective surfaces. They are ductile and malleable, good conductor of heat and electricity, and they usually have high melting points. Copper, silver, gold, iron and aluminium are familiar examples of metals.

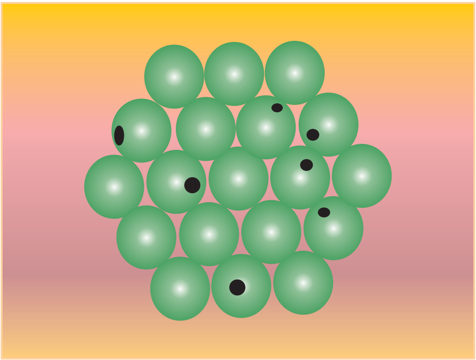


Figure 3.26 Model of metallic crystal.

Table 3.2 Comparison of the four types of crystals

Type of Solid	Interaction	Properties	Examples
Ionic	Ionic	High melting point, brittle, hard	NaCl, MgO
Molecular	Hydrogen bonding, Dipole-Dipole, London dispersion	Low melting point, non-conducting	H_2, CO_2
Network	Covalent bonding	High melting point, hard, non-conducting	C (diamond), SiO_2 (quartz)
Metallic	Metallic bonding	Variable hardness and melting point (depending upon strength of metallic bonding), conducting	Fe, Mg

Exercise 3.18

Match the substances from list A with the best suited characteristics given in list B and justify your answer.

List A Substances		List B Characteristics
a Fe	a	Forces of attractions are between positive ions and 'sea of electrons'
b I_2	b	High boiling point due to strong covalent bonds
c H_2O	c	High boiling point due to hydrogen bond
d SiO_2	d	Weak van der Waal's forces
e Na	e	Giant metallic lattice, ions packed together very closely leading to high density
	f	Non-polar solvent

Unit Summary

- *Lewis symbols of representative elements are related to their location in the periodic table. The lattice energy and enthalpy of formation of an ionic compound, together with other atomic and molecular properties, can be related in a thermochemcial cycle called Born-Haber cycle.*
- *A covalent bond is created by the sharing of an electron-pair between atoms.*
- *In a Lewis structure representing covalent bonds, electron-pairs are either bonding-pairs or lone-pairs.*
- *In a covalent bond between atoms of different electronegativity, electrons are displaced toward the atom with the higher electronegativity. In terms of electronegativity differences chemical bonds vary over the range: non polar to polar covalent to ionic.*

- *In some cases of covalent bonding, one atom appears to provide both electrons in the bonding pair; the bond is known as coordinate-covalent bond.*
- *Bonded atoms may share more than one pair of electrons between them, giving rise to multiple covalent bonding.*
- *In the phenomenon of resonance, two or more Lewis structures have the same skeletal structure but different bonding arrangements. The best description of the resonance structure (resonance hybrid) is obtained by combining plausible structures (contributing structures).*
- *Exceptions to the octet rule are found in odd-electron molecules and molecular fragments called free radicals. A few structures appear to have too few electrons to complete all the octets. Some structures appear to have too many. In the latter case, a central atom may employ an "expanded" octet with five or six electron-pairs.*
- *Valance shell electron pair repulsion theory (VSEPR) predicts the geometrical structures of molecules and polyatomic ions based on mutual repulsions among valance shell electron groups.*
- *Multiple bonds, whether they consist of four electrons (double bond) or six electrons (triple bond), are treated as one electron set.*
- *The separation of the centres of positive and negative charge in a polar covalent bond creates a bond moment. Whether a molecule as a whole is polar, that is, whether there is a resultant dipole moment, is established by bond moments and molecular geometry.*
- *A symmetrical distribution of identical bond moments about a central atom results in a cancellation of all bond moments, with the result that the molecule is nonpolar, as in the case of* CCl_4..
- *In the valence bond method (VB) a covalent bond is viewed as the overlap of atomic orbitals of the bonded atoms in a region between the atomic nuclei.*
- *Molecular geometry is determined by the spatial orientations of the atomic orbitals involved in bonding.*
- *The VB method often requires that bonding atomic orbitals be hybridized in order to rationalize known structures of molecules. A hybridized orbital is some combination of s, p and d orbitals, such as sp,* sp^2, sp^3,

sp^3d and sp^3d^2. The geometric distribution of hybridized orbitals in the valence bond method is the same as the electron set geometry proposed by VSEPR theory.

- *Hybrid orbitals overlap in the usual way (end-to-end) and form σ bonds. Unhybridized p orbitals overlap in a side-by-side manner and give rise to π bonds. A double bond consists of one σ bond and one σ bond; a triple bond, one σ bond and two π bonds.*
- *Acceptable solutions to wave equations written for the electrons in a molecule are called molecular orbitals (MO). The two main types of MOs are bonding molecular obitals, which concentrate electron charge density between atoms or just above and below the imaginary line joining the two nuclei and antibonding molecular orbitals, which concentrate electron charge densities away from the intermolecular bonding region.*
- *Electrons can be assigned to molecular orbitals by the scheme similar to the aufbau process. MO theory provides more satisfactory descriptions for certain structures than does the VB method, for example, some odd - electrons species and the O_2 molecule.*

Check list

Key terms of the unit

- *Anion*
- *Atomic orbital*
- *Covalent bond*
- *Crystal*
- *Delocalisation of electrons*
- *Dipole*
- *Dipole moment*
- *Double bond*
- *Electric charge*
- *Ionic bond*
- *Ionization*
- *Kinetic energy*
- *Lattice*
- *London dispersion forces*
- *Molecule*
- *Molecular orbital*
- *Noble gases*
- *Potential energy*
- *Single bond*
- *Substance*
- *Triple bond*
- *Unit cell*
- *Valence electron*
- *Valence bond theory*
- *Van der Waals force*

REVIEW EXERCISE

Part I: Multiple Choice Questions

1. "Two atoms each provide two electrons that are shared by the two atoms" This is a description of a
   - a triple covalent bond
   - b coordinate covalent bond
   - c double covalent bond
   - d single covalent bond
2. A non-metal usually forms two covalent bonds in its compounds. How many electrons will it have in its valence shell?
   - a 2
   - b 4
   - c 6
   - d 8
3. The noble gases do not usually form chemical compounds because:
   - a they have very stable nuclei.
   - b the bonds between their atoms are very strong.
   - c they already have paired valence shell electrons.
   - d they are not polar.
4. Which of the following compounds contain both ionic and covalent bonds?
   - a CO_2
   - b Cl_2O
   - c Na_2CO_3
   - d $BaCl_2$
5. Which of the following molecules would you expect to be non-planar?
   - a CH_4
   - b BCl_3
   - c XeF_4
   - d HCHO
6. If a molecule has a trigonal pyramidal shape, how many non-bonding pairs of electrons are present in the valence shell of the central atom?
   - a 1
   - b 2
   - c 3
   - d 4
7. Of the following, the most polar bond is:
   - a P – Cl
   - b Si – F
   - c S – O
   - d C – N

8. Carbon and chlorine form a series of compounds: CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4. Which of these will be polar:

   a CCl_4 only

   b CH_3Cl and $CHCl_3$ only

   c CH_3Cl, CH_2Cl_2 and $CHCl_3$ only

   d CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4

9. The carbon atoms in ethane (C_2H_6), ethene (C_2H_4) and ethyne (C_2H_2) provide, respectively, examples of the three common types of hybridization corresponding to:

   a sp, sp^2, sp^3

   b sp^3, sp^2, sp

   c sp, sp^3, sp^2

   d sp^3, sp, sp^2

10. Which of the following correctly describes a π bond?

    a It is formed by the end-to-end interaction of *p*-orbitals and has a low electron density on the internuclear axis.

    b It is formed by the parallel interaction of *p*-orbitals and has a high electron density just above and below the internuclear axis.

    c It is formed by the interaction of *s*-orbitals and has a low electron density on the internuclear axis.

    d It is formed by the interaction of *s*-orbitals and has a high electron density on the internuclear axis.

11. Which of the following species cannot be adequately described by a single Lewis structure?

    a OH^-

    b C_2H_2

    c NH_4^+

    d HCO_3^-

12. In which of the following compounds would inter-molecular hydrogen-bonding occur?

    a HCHO

    b PH_3

    c CH_3OH

    d $COCl_2$

13. Which of the following molecules would you expect to have the highest boiling point?

    a $CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$

    b $CH_3–CH(CH_3)–CH_2–CH_2–CH_3$

    c $CH_3–CH_2–CH(CH_3)–CH_2–CH_3$

    d $CH_3–C(CH_3)_2–CH_2–CH_3$

14. Which of the following molecules possesses the strongest forces between the molecules?

    a N_2

    b $CH_3–CH_3$

    c H_2CO

    d CH_4

15. Which one of the following usually produces the weakest interaction between particles of similar molar mass?

    a Van der Waals forces

    b Dipole-dipole forces

    c Covalent bonds

    d Hydrogen-bonding

16. The hydrogen bonding is not significant in:

    a DNA

    b protein

    c ice

    d poleythene

17. A gas is likely to:

    a have its atoms held together by metallic bonds.

    b have a giant covalent structure.

    c be a compound of a metal.

    d have a molecular covalent structure.

18. If an element in group IIA of the periodic table formed a compound with an element in group VIIA of the periodic table, the compound formed is likely to:

    a be a crystalline solid

    b dissolve in non-polar solvents

    c have a low boiling point

    d conduct electricity in the solid state

19. Which of the following substances would you expect to have the lowest boiling point?

    a CsCl

    b $SrSO_4$

    c Sc_2O_3

    d $AsCl_3$

20. Which of the following would not conduct an electric current?

a solid mercury
b Aqueous sodium chloride
c liquid sodium chloride
d solid sodium chloride

Part II: Answer the following questions:

21. Name the following compounds:

a KBr
b $Al\ I_3$
c Li_3N
d BeO
e BaS

22. Predict the shape for the following molecules:

a SiF_4
b PCl_3
c H_2S
d NF_3
e CCl_4
f PCl_5

23. Draw Lewis structures and predict the shapes, giving approximate bond angles for:

CH_3^+, CH_3^-, $\cdot CH_3$ (methyl radical), HCN, ICl_2, NH_2^-, NO_2, ClO_2.

24. Classify the given molecules as polar or non-polar:

a SiF_4
b NF_3
c PCl_3
d H_2S
e CCl_4
f CO_2

25. Which atom (if any), in each of the following bonds would you expect to carry a partial negative charge?

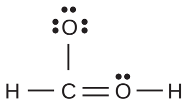
a H – N
b S – S
c O – P
d C – F
e B – O
f I – F

26. Draw the Lewis structure for the given molecules and state whether the molecule is polar or non-polar:

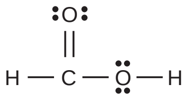
a PF_4^-
b ICl_4^-
c N_2F_2 (*2 forms possible*)

27. Boron trifluoride can react with a fluoride ion to give the tetrahedral BF_4^- ion. What type of hybridization would you expect the boron to have in BF_4^-?

28. Carbon and oxygen can bond either by a single bond (as in CH_3–OH), a double bond (as in O=C=O), or a triple bond (as in HC≡CH).
    - a Describe these three types of bonds in terms of σ-bonds and π-bonds.
    - b How would you expect the length of the carbon-oxygen bond to vary in the three given examples?
29. Explain the following in terms of the intermolecular forces that exist in them:
    - a Water is a liquid at room temperature and atmospheric pressure, but hydrogen sulphide is a gas.
    - b At room temperature and atmospheric pressure chlorine is a gas, bromine is a liquid and iodine is a solid.
    - c Pentan-1-ol boils at 137°C, where as pentan-3-ol boils at 116°C.
    - d The boiling point of sulphur dioxide is 24°C higher than that of chlorine.
30. Of the two possible valence-bond formulas for formic acid (HCO_2H) , which one is the more reasonable structure?



(a)

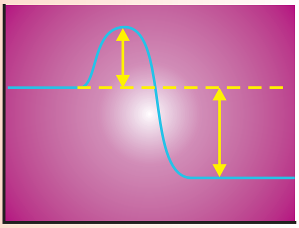


(b)

31. Draw the correct valence-bond formula for hydrazine (N_2H_4).
32. Draw the resonance hybrid of SO_2.
33. Based on the VB approach, predict the shape of a ClO_3^- ion.
34. The molecular orbital description of NO is similar to that of O_2 except that the energies of the oxygen atomic orbitals are slightly lower than those of nitrogen atomic orbitals and NO molecule contains different number electrons than O_2.
    - a Draw an energy diagram to show how the atomic orbitals of N and O combine to form molecular orbitals of NO.
    - b How many unparied electrons are present in the NO molecule?
    - c What is the bond order in NO molecule?
    - d Is NO paramagnetic or diamagnetic?
35. List the following in order of increasing O – O bond length : O_2, O_2^+, O_2^-
36. Show the direction of the bond moment (dipole moment) in each of the following bonds:

N – F, N – H, N – Si, N – O

UNIT 4



Chemical Kinetics

Unit Outcomes

At the end of this unit, you should be able to:

- *explain what is meant by reaction rate and perform activities that determine it;*
- *demonstrate an understanding of the dependence of reaction rate on the nature of reactants, the surface area of solid reactants, the concentration of the reactants, temperature of a system and the presence and nature of catalysts;*
- *determine reaction rates, using experimental data and calculations;*
- *describe how reaction rate theories (collision theory and transition-state theory) explain changes in reaction rates;*
- *determine the rate laws and order of reactions from data on initial concentrations and reaction rates;*
- *understand that most reactions occur as a series of elementary steps in reaction mechanisms;*
- *appreciate the importance of chemical kinetics in industry and in living organisms; and*
- *demonstrate scientific enquiry skills, including observing, predicting, comparing and contrasting, communicating, asking questions, drawing conclusions, applying concepts, relating cause and effect, making generalizations and problem solving.*

MAIN CONTENTS

Start-up Activity

Form a group and determine the approximate time taken for completion of following chemical changes:

a Burning of a piece of paper.

b Conversion of milk to curd.

c Ripening of grapes.

d Charring of sugar.

e Formation of fossil fuels.

Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Why do some chemical reactions proceed quickly, whereas others require days, months or even years to give products?
2. Is the rate of reaction (speed) fixed for a particular type of reaction?
3. How will the rate of reaction get altered when subjected to small changes in temperature, concentration etc.?
4. How can we measure the rate of reaction?

5. Is the rate of reaction defined for both:
   i) reversible and irreversible reactions, and
   ii) slow and fast reactions.
6. How does a study of the rate of a chemical reaction inform us about the way in which reactants combine to form products?

INTRODUCTION

In Grade 9 chemistry, you learned that not all chemical reactions proceed at equal speed. For example, rusting of iron could start while rippening of fruits may be completed in a few days. On the other hand, weathering of stone may take more than a decade and the brakedown of plastics in the environment takes more than hundred years. However, other reactions, like the combustion of gasoline or the explosion of gunpowder occur in a few seconds. Can you add more examples from your daily life?

Now, let us define Chemical kinetics. Chemical kinetics is the area of chemistry concerned with the speeds, or rates, at which reactions occur. The word "kinetic" suggests movement or change. Chemical kinetics refers to the rate of reaction, which is the change over times in the concentration of a reactant or a product.

In this unit, you will study the fundamental concepts of chemical kinetics. You will explore rate of reaction, factors affecting rate of reaction, theories of rate of reaction, rate equations or rate laws, and reaction mechanisms.

Historical Note

Peter Waage (right) and Cato Guldberg (left)

Peter Waage (1833–1900) and Cato Guldberg (1836–1902) were Norwegian chemists. They pioneered the development of chemical kinetics in 1864 by formulating the law of mass action.

4.1 RATE OF REACTION

At the end of this section, you should be able to:

- define chemical kinetics;
- define reaction rate;
- express reaction rate in terms of the disappearance of the reactants and the appearance of the products;
- perform an activity to measure rate of reaction;
- calculate a reaction rate from given data;
- list the factors that affect reaction rate;
- explain how the nature of reactants, the surface area of solid reactants, temperature and concentration or pressure affect rate of reaction, by giving examples;
- explain activation energy;
- define catalyst, positive catalyst and negative catalyst;
- distinguish between homogeneous and heterogeneous catalysis;
- distinguish between biological and non-biological catalysts;
- draw an energy diagram that represents activation energy and shows the effect of catalysts;
- distinguish between homogeneous and heterogeneous reactions; and
- perform an activity to show the effect of the nature of reactants, surface area, concentration, temperature and catalyst on reaction rate.

Activity 4.1

Form a group and discuss the following:

For the given reaction,

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$$

1. What happens to the concentration of a reactant as the time of reaction increases?
2. What about the concentration of a product over the time?
3. In your notebook, sketch a graph of changes in reactant and product concentration over time. In order to do this write time as the x-axis and concentration as the y-axis?
4. What do you learn from the graph?

Share your ideas with the rest of the class.

From your background knowledge of chemistry, do you remember the definition of a chemical reaction? What is the difference between reversible and irreversible chemical reactions? Consider a flask containing hydrogen, iodine, and hydrogen iodide. The hydrogen iodide, HI is decomposing more rapidly than the H_2 and I_2 can combine to produce it. The chemical equation representing the formation of HI from this reaction of hydrogen and iodine is represented as:

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

The rate of appearance of HI in the above reaction is defined as the rate of reaction from left to right.

For the diappearnace of HI,

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

the rate of disappearance of HI is then defined as the rate of reaction from right to left.

How do you think that the rate of reaction is measured?

Rate of reaction is the change in concentration of a reactant or a product over a given period of time. During the course of a reaction, the concentrations of the reactants decrease while those of the products increase. Thus, the rate of a reaction is calculated by dividing the change in the concentrations of reactants or products by the time taken for the change to occur.

For a simple reaction,

$$A \longrightarrow B$$

the rate of reaction is expressed in terms of a reactant concentration as

$$r = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_f - [A]_i}{\Delta t} \qquad ...(4.1)$$

where r is rate of reaction, A is a reactant, B is a product, $[A]_i$ and $[A]_f$ are initial and final concentration of A respectively, $\Delta[A]$ is change in concentration of A and Δt is the change in time. Note that concentration is usually expressed in mole per litre.

From equation 4.1, can you determine the unit for expressing rate of reaction?

The rate of a reaction can be expressed in units of mol L^{-1} s^{-1}. The final concentration of the reactant, $[A]_f$, is smaller than the initial concentration of the reactant, $[A]_i$ Thus, the difference, $\Delta[A] = [A]_f - [A]_i$, is negative. This indicates that the reactant is being consumed. However, the rate of a reaction is a positive quantity. Thus, a negative sign is introduced in the rate expression to make the rate positive.

Can you write a rate of reaction in terms of concentration of a product?

In terms of product concentration, the rate of a reaction is given by:

$$r = \frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{[\mathrm{B}]_\mathrm{f} - [\mathrm{B}]_\mathrm{i}}{\Delta t} \qquad \text{...(4.2)}$$

where [B] is the molar concentration of a product in moles per litre, mol L^{-1}. For a given product, the final concentration of B, $[B]_f$, is greater than the initial concentration of B, $[B]_i$. Thus, the difference, $\Delta B = [B]_f - [B]_i$ is positive, and the rate of a reaction is also positive. Therefore, there is no need to introduce a negative sign to the rate expression when rate of a reaction is calculated by using product concentration. This change can be shown using a graph.

Reaction Rate and Stoichiometry

You have seen that, for stoichiometrically simple reactions of the type $A \longrightarrow B$, the rate of reaction can be expressed either in terms of the decrease in reactant concentration over time, $-[A] / \Delta t$, or in terms of the increase in product concentration with time, $\Delta[B]/\Delta t$. For more complex reactions, you must be careful in writing the rate expressions. Consider, for example, the reaction

$$2A \longrightarrow B$$

For two moles of A that disappear one mole of B is formed. That is, the rate of disappearance of A is twice as the rate of appearance of B. The reaction rate may be written as:

$$r = -\frac{1}{2}\frac{\Delta[\mathrm{A}]}{\Delta t} \quad \text{or} \quad r = \frac{\Delta[\mathrm{B}]}{\Delta t}$$

In general, for the reaction

$$\mathrm{aA + bB \rightarrow cC + dD}$$

The rate of reaction is given by:

$$r = -\frac{1}{\mathrm{a}}\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{1}{\mathrm{b}}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{\mathrm{c}}\frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{1}{\mathrm{d}}\frac{\Delta[\mathrm{D}]}{\Delta t} \qquad \text{...(4.3)}$$

where r is the rate of reaction, A and B are reactants, C and D are products, and a, b, c, d are stoichiometric coefficients.

Example 4.1

1. Write the rate expressions for the following reactions, in terms of the disappearance of the reactants and the appearance of the products:

a $I^-(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + OI^-(aq)$

b $3O_2(g) \rightarrow 2O_3(g)$

c $4NH_3\,(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Solution:

a Since all of the stoichiometric coefficients are equal,

$$r = -\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[OCI^-]}{\Delta t} = \frac{\Delta[CI^-]}{\Delta t} = \frac{\Delta[OI^-]}{\Delta t}$$

b Here, the coefficients are 3 and 2, so,

$$r = -\frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[O_3]}{\Delta t}$$

c In this reaction

$$r = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

2. In the reaction of nitric oxide with hydrogen,

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

If the rate of disappearance of NO is 5.0×10^{-5} mol $L^{-1}s^{-1}$,

What is the rate of reaction for the formation of N_2?

Solution:

The rate of reaction for the formation of N_2

$$r = \frac{\Delta[N_2]}{\Delta t} = -\frac{1}{2}\frac{[NO]}{\Delta t} = ½\ (5.0 \text{ x } 10^{-5} \text{ mol } L^{-1}s^{-1})$$

$$r = 2.5 \text{ x } 10^{-5} \text{ mol } L^{-1}s^{-1}$$

Exercise 4.1

1. Define the rate of reaction.
2. For the reaction:

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

express rate of reaction in terms of the concentration of:

a) H_2

b) HI

3. For the reaction:

$$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$$

a) express the rate of reaction in terms of the concentration of NOCl.

b) relate the rate of reaction of NOCl with the rate of reaction of NO and Cl_2.

4. The reaction for the formation of ammonia is given as:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Write the rate reaction for:

a) the formation of NH_3.

b) the disappearance of N_2 and H_2.

4.1.1 Determination of Rate of Reaction

You studied in the previous grade that there are different ways in which reactions are monitored. These include change of colour, volume of gas evolved, amount of precipitate formed and loss or gain of mass. In addition, you learned how to draw a graph showing how the rate of a chemical reaction changes over time and how the rate relates to the slope.

Activity 4.2

Form a group and discuss the following:

The results obtained during the reaction between excess of powdered calcium carbonate and hydrochloric acid, are given in the following table:

$$CaCO_3(s) + HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Volume of CO_2 / cm^3	0	20	35	47	56	64	69	73	77	80
Time/s	0	10	20	30	40	50	60	70	80	100

a Plot these data on graph paper.

b At what time is the reaction most rapid?

c What is the rate of reaction after 50 seconds?

d What volume of gas has formed after 15 seconds?

e How long did it take for 40 cm^3 of carbon dioxide to form?

f Why does the rate of reaction gradually slow down?

Share your ideas with the rest of the class.

The rate of reaction can be determined both quantitatively and qualitatively. Qualitatively, an idea about the rate of reaction can be obtained by observing either the speed of disappearance of the reactants or the speed of appearance (formation) of the products.

Example 4.2

In aqueous solutions, molecular bromine reacts with formic acid (HCOOH) as follows:

$$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(aq)$$

Molecular bromine is reddish-brown in colour. All the other species in the reaction are colourless. As the reaction progresses, the concentration of Br_2 steadily decreases and the colour fades. Measuring the change (decrease) in bromine concentration over time measuring at some initial time and then again at some final time) allows us to determine the average rate of the reaction during that interval.

$$r = -\frac{\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

where r is the average rate. Use the data provided in Table 4.1.

Table 4.1 Rates of reaction between molecular bromine and formic acid at 25 °C

Time (s)	$[Br_2]$ (M)	Rate (M/s)	$k = \dfrac{\text{rate}}{[Br_2]}$ (s)
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.0596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.0500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.0420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.0353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.0296	1.04×10^{-5}	3.51×10^{-3}

Now, you can calculate the average rate at the end of the first 50-second (s) time interval, as follows:

$$r = -\frac{(0.0101 - 0.0120)\text{M}}{50.0\text{ s}} = 3.80 \times 10^{-5}\ \text{M/s}$$

If the first 100 s is chosen as the time interval, the average rate will be given by:

$$r = -\frac{(0.00846 - 0.0120)\text{M}}{100.0\text{s}} = 3.54 \times 10^{-5}\ \text{M/s}$$

The above calculations demonstrate that the average rate of reaction depends on the time interval we choose. Thus, in general, the rate of reaction at the begining is fast and it decreases as the reaction proceeds.

What could be the possible reason for this decrease in the rate of reaction?

Exercise 4.2

Consider the reaction:

$$2C_2H_4(g) \rightarrow C_4H_8(g).$$

From the experimental data given in table, plot a graph for the consumption of ethylene, C_2H_4, versus time.

a Calculate the rate of reaction between the time interval 10 s to30 s.

b Calculate the rate of reaction at 45 s.

time s	0	10	20	40	60	100
$[C_2H_4]$ mol L^{-1}	0.884	0.621	0.479	0.328	0.250	0.169

Instantaneous rate of reaction is defined as the rate of a reaction for a given instant of time and it is calculated by drawing a tangent to the graph at that instant of time.

Earlier, we measured the rates of reaction that occurred in a few seconds. We can also measure the rates of very fast reactions occurring in micro (10^{-6}) or nano (10^{-9}) seconds. For example, the rate of electron transfer in photosynthesis can be measured.

The following experiment demonstrates the rate of reaction between marble chips ($CaCO_3$) and dilute hydrochloric acid, HCl.

Experiment 4.1

Measuring Rate of Reaction

Objective: To measure the rate of reaction between marble chips ($CaCO_3$) and dilute HCl.

Apparatus: Direct reading balance, 100 mL conical flask, stopwatch, cotton wool.

Chemicals: 2 M dilute HCl solution, and marble chips/$CaCO_3$.

Procedure:

1. Set up the apparatus as shown in Figure 4.1, but without the marble chips at first.
2. Add 20 g of pure marble chips, in a clean 100 mL conical flask.
3. Add 40 mL of 2 M dilute hydrochloric acid to the conical flask.
4. Plug the cotton wool in position immediately.
5. Read the mass of the flask and its contents and start the stopwatch.
6. Record the mass at one minute intervals for 10 minutes.

Figure 4.1 Laboratory set up for the measurement of rate of reaction.

Observations and analysis:

1. Use the following table to record your observations.

Time (minutes)	0	1	2	3	4	5	6	7	8	9	10
Mass (g)											
Decrease in mass (g)											

Plot a graph with time (minutes) on the horizontal axis and rate on the vertical axis. Draw a smooth curve through as many points as possible. Note that in this experiment change in mass is proportional to change in concentration.

2. What happens to the mass during the reaction? Explain this with the help of balanced equation.
3. What information can be obtained from the slope of this graph at any point?
4. Why is the graph:

a steep at the start of the reaction?

b less steep in the middle of the reaction?

c horizontal at the end of the reaction?

5. Calculate:

   a The average rate of the reaction.

   b The rate of reaction at 2 minutes.

6. Describe how the rate of reaction changes with time.

7. Can we measure the rate of this reaction by measuring the amount /volume of CO_2 evolved?

8. Draw a graph of the expected result by plotting volume of CO_2 evolved vs time.

Exercise 4.3

For the reaction,

$$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

The rates of reaction of $N_2O_5(g)$, and $NO_2(g)$ as a function of time at 45 °C is given in the table below

Time (min)	N_2O_5 (M)	NO_2 (M)
0	1.24×10^{-2}	0
10	0.92×10^{-2}	0.64×10^{-2}
20	0.68×10^{-2}	1.12×10^{-2}
30	0.50×10^{-2}	1.48×10^{-2}
40	0.37×10^{-2}	1.74×10^{-2}
50	0.28×10^{-2}	1.92×10^{-2}

Use the data given in the table and calculate the rate of:

a formation of NO_2 over the first 10 minutes.

b decomposition of N_2O_5 during the time interval t = 30 min to t = 50 minutes.

4.1.2 Factors Influencing the Reaction Rates

Activity 4.3

Form a group and try to dissolve 2 teaspoons of sugar crystals in coldwater, in warm water and in hot water simultaneously. Repeat the same steps using sugar powder. You may also try the same activity with oil, instead of water. Now, discuss each of the following questions and share your findings with the rest of the class.

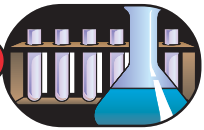
1. Why do you think sugar crystals dissolve more easily in hot water than in cold water?
2. Explain why powdered sugar dissolved easily as compared to equivalent amounts of sugar crystals?

In general, different chemical reactions have different rates. Even a chemical reaction involving the same reactants may have different rates under different conditions. Change in temperature, concentration, nature of reactant, surface area and availability of a catalyst, result in changes in rate of reaction.

Consider the Experiment 4.2 to study the effect of the nature of reactants on rate of reaction.

i) Nature of Reactants

Experiment 4.2



Effect of Nature of Reactants on Rate of Reaction

Objective: To study the effect of nature of reactant for the reaction of copper and magnesium metals with hydrochloric acid.

Apparatus: Balance, test tubes, test tube stand.

Chemicals: Copper (Cu), magnesium (Mg), 2 M hydrochloric acid (HCl).

Procedure:

1. Measure equal masses of copper and magnesium metals using a balance.
2. Record the weighed mass of these metals and add each to separate test tubes.
3. Assemble the test tubes as shown in Figure 4.2.
4. Add equal volume of 5 mL of 1 M HCl to both the test tubes. Be sure to wear your safety goggles and gloves.

5. Observe relative rates of reaction in both test tubes and record your observations.

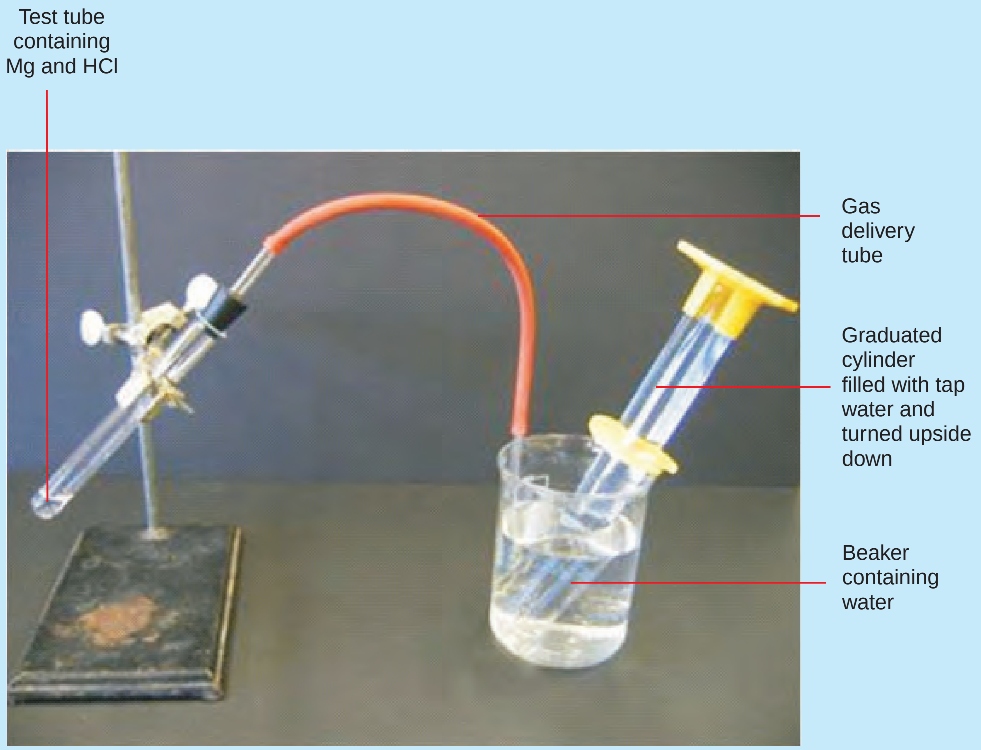


Figure 4.2 Reaction of magnesium with HCl.

Observations and analysis:

1. Which of these two metals, copper or magnesium, reacts faster? Why?
2. Write the balanced chemical equation for the reaction of copper and magnesium with HCl.
3. What do you learn from this experiment?
4. Perform a similar activity using different metals such as aluminium, and zinc. In which case do you expect the reaction to be faster and why?

The rate of a reaction depends on the chemical nature of the substances participating in the reaction. The combination of two oppositely charged ions usually occurs very rapidly. For example, the reaction of an acid with a base is,

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

The acid-base reaction of HCl and NaOH is much faster than the decomposition of hydrogen peroxide, which involves the reorganization of molecules.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Even similar reactions may have different rates under the same conditions. For example, consider the reaction of calcium with water compared with the reaction of iron with water. The reaction of calcium with cold water is moderate, while that of iron is very slow infact iron reacts with steam to form iron oxide.

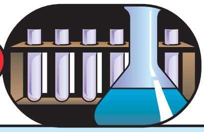
$$3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

Consider the Experiment 4.3 to study the effect of surface area on rate of reaction.

ii) Surface Area of Reactants

Experiment 4.3



Effect of surface Area on Reaction Rate

Objective: To study the effect of surface area of reactants on the rate of reaction using cube chalk and powdered chalk with dilute hydrochloric acid.

Apparatus: Direct reading balance, 100 mL conical flask, stopwatch, cotton wool.

Chemicals: Cube chalk, powered chalk and 2M dilute HCl solution

Procedure: Repeat Experiment 4.1 but use 20 g of small cubical chalk and then powdered chalk in place of marble chips.

Observations: In which case is the evolution of gas is faster?

Observations and analysis:

1. Compare the rate curve, average rate and reaction rate at 2 minutes with that of Experiment 4.1. Explain your observations.
2. Sketch a graph for the consumption of each size of chalk (cube chalk and powdered chalk) against time on the same graph sheet.
3. State the conclusion of the experiment.

Which form of Zinc metal is easier to dissolve in dilute HCl, large pieces of Zn or powdered Zn? Why?

A reaction between substances that are in different physical phases (solid, liquid, gas) is called *a heterogeneous reaction*. In this case, bringing the reacting molecules or ions together may be difficult. For example, the reaction between steam and red hot iron, proceeds very slowly if the iron is in one large block, but it goes rapidly if the metal is powdered and spread out so as to expose a large surface to the steam.

$$3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

In general, the area of contact between the phases ditermines the rate of reaction in heterogenous reaction. When the size of particles is minimized, contact between the atoms, ions, or molecules in the solid state maximizes with those in a different phase.

A reaction of substances when both are in the gaseous or liquid phase, is referred to as a homogeneous reaction. The question of contact between the reactive molecules in a homogeneous reaction is not an important one, for the molecules and ions are free to move and collisions are frequent.

Consider Experiment 4.4 to study the effect of concentration of acid on the rate of reaction between $CaCO_3$ and hydrochloric acid.

Exercise 4.4

1. Write the factors affecting the rate of chemical reaction.
2. Describe the differences between homogeneous reaction and heterogeneous reaction.

iii) Concentration of Reactants

Experiment 4.4

Effect of Concentration on Reaction Rate

Objective: To study the effect of concentrations of hydrochloric acid on rate of reaction with marble chips.

Apparatus: Direct reading balance, 100 mL conical flask, stopwatch, cotton wool

Chemicals: 1 M HCl, 2 M HCl dilute solutions and marble chips ($CaCO_3$).

Procedure:

Repeat experiment 4.1 but use 1 M dilute HCl in place of 2 M dilute HCl.

Observations and analysis:

1. Compare the rate of reaction with that in Experiment 4.1. Which reaction is more vigorous? Explain.
2. Which of the two reactions will produce more carbon dioxide? Explain your answer.
3. What would happen to the rate curve and average rate if:
   a 1M HCl is replaced with 4 M dilute HCl? Explain.
   b 1M HCl is replaced with 0.5 M dilute HCl? Explain.
4 Sketch a graph for each of 0.5 M, 1 M, 2 M and 4 M dilute HCl against time on the same graph sheet.

Why does wood burn more rapidly in pure oxygen than in air?

When the concentration of one or more reactants increases, rate of reaction increases. This is because increasing the concentration produces more contacts between the reacting particles, which results in increasing the rate of reaction. In the case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction. However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.

The examples of rate of reaction being affected by different factors can be seen in both biotic and abiotic components. For example, growth of cancer cells depends on the nutrient levels, temperature, pH, etc. The rate of growth of cancer cells has been measured as a function of glucose (nutrient) concentration. The cells grow as the glucose concentration decreases.

In Experiment 4.5, you will study the effect of temperature on the rate of reaction of $Na_2S_2O_3$ with HCl.

iv) Temperature of Reactants

Experiment 4.5

Effect of Temperature on Reaction Rate

Objective: To study the effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid.

Apparatus: 100 mL beakers, test tubes, thermometers, white paper, pencil.

Chemicals: 0.5 M dilute HCl solution, 0.1 M $Na_2S_2O_3$ solution, pieces of ice.

Procedure:

1. Take 25 mL of 0.1 M $Na_2S_2O_3$ solution in a test tube and 25 mL of 0.5 M HCl solution in another test tube.
2. Prepare 3 such sets and maintain them at different temperatures.

   Set (*i*) at 0°C [by keeping them in a ice bath as shown in Figure 4.3 (a)].

   Set (*ii*) at room temperature.

   Set (*iii*) at 40°C (by heating the two solutions in a water bath).
3. Put a cross sign on a white cardboard and place a clean dry 100 mL beaker above it.
4. Now, pour the contents of set (*i*) in the beaker and start a stopwatch immediately.
5. Carefully stir the mixture with thermometre and record the time taken for the cross to disappear [Figure 4.3 (b)].
6. Repeat steps 3, 4, and 5 with set 2 and set 3 respectively.
7. Tabulate your results as temperature in °C versus time in minutes.

Observations and analysis:

1. What was the appearance of the mixture at the start of the reaction, and at the end of the reaction? Explain the changes using the equation for the reaction.
2. Plot the graph of time (minutes) on the horizontal axis against rate on the vertical axis.

3. Under which condition of temperature does the cross take:
   a the shortest time to disappear, and
   b the longest time to disappear.
4. Draw a conclusion about the relationship between the average reaction rate and temperature.

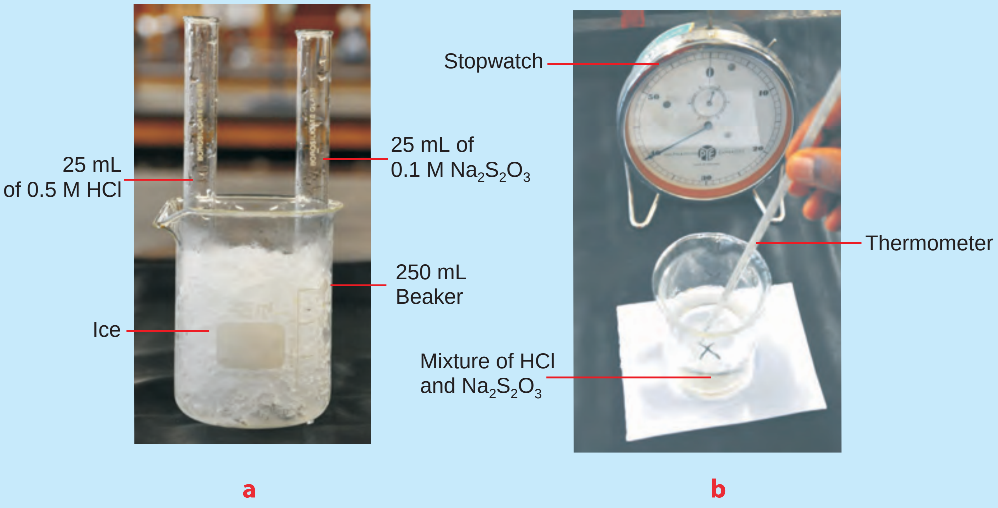


Figure 4.3 Laboratory Setup for the study of the effect of temperature on reaction of $Na_2S_2O_3$ and HCl.

Temperature usually has a major effect on the rate of reaction. Molecules at higher temperatures have more thermal energy. Generally, an increase in the temperature of a reaction mixture increases the rate of reaction of chemical reactions. This is because as the temperature of the reaction mixture raises, the average kinetic energy of the reacting particles increases. So, they collide more frequently and with greater energy.

The effect of temperature on rate of reaction can be experienced in our dailylife. For example,

a the food is kept in refrigerator to slow down the rate of decomposition of food; and

b during heart surgery, the body of patient is cooled to slowdown the rates of biological reactions.

Temperature not only affects the rate of reaction but can even change the course of a reaction. For example,

At 200°C,

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$$

At even higher temperature,

$$2NH_4NO_3(s) \rightarrow N_2(g) + O_2(g) + 4H_2O(g)$$

Now, you will perform Experiment 4.6 to study the effect of a catalyst on the rate of decomposition of hydrogen peroxide, H_2O_2.

v) Presence of a Catalyst

Effect of Catalyst on Rate of Reaction

Experiment 4.6

Objective: To investigate the effect of a catalyst on rate of reaction of decomposition reaction of hydrogen peroxide.

Apparatus: Conical flask, gas syringe, delivery tube.

Chemicals: 0.5% by volume H_2O_2 solution, MnO_2.

Procedure:

1. Set-up the apparatus as shown in Figure 4.4. Set the volume of the gas syringe at 0 mL. Add 25.0 mL of 0.1 M H_2O_2 solution, but without manganese (IV) oxide, MnO_2, and start stopwatch immediately.
2. Record the volume of gas collected in gas syringe at minute intervals until each reaction is almost complete.
3. Repeat steps 1 and 2 with 1 g of MnO_2.

Observations and analysis:

1. Identify the gas and write a balanced chemical equation for the reaction.
2. Under which condition does gas syringe contains more of the gas at any one time? Give an explanation for this observation.
3. Describe the appearance of MnO_2 before and after the reaction.
4. Plot graphs of rate on the vertical axis and time (minutes) on the horizontal axis for two different sets of readings. Which set of reading were used? Why?
5. Draw conclusion about the reaction rate:
   a in the presence of a catalyst;

b in the absence of a catalyst.

Fig 4.4 Investigating the effect of managanese (IV) oxide on hydrogen peroxide.

How do inhibitors extend the shelf-life of a package of food?

A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with a lower activation energy, E_a, which is the minimum energy needed to start a chemical reaction. A catalyst may undergo physical changes and it may even form temporary chemical bonds with the reactants but it is recovered unchanged in original form at the end of the reaction. Although a catalyst speeds up the reaction, it does not alter the position of equilibrium. The effect of catalysts on the rate of chemical reaction is illustrated in Figure 4.5.

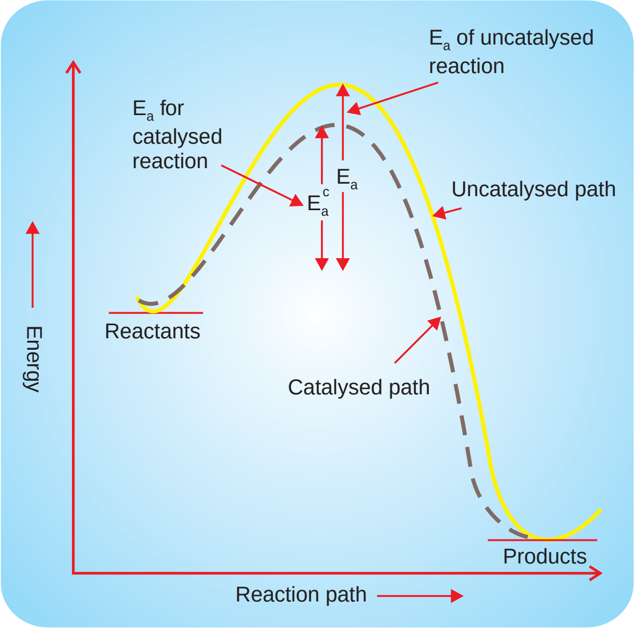


Figure 4.5 Comparsion of activation energies of a catalysed and an uncatalysed reaction.

Chemical catalysts can be either positive or negative. Positive Catalyst increases the rate of reaction by lowering the Activation Energy, E_a.

Example (1) : $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$; $V_2O_5(s)$ as catalyst.

Negative Catalyst or Inhibitors decreases the rate of reaction by increasing the value of E_a.

Example (2) : $OCl^-(aq) + I^-(aq) \rightarrow OI^-(aq) + Cl^-(aq)$; $OH^-(aq)$ as inhibitor.

Example(1) represents heterogeneous catalysts as state of reactants and catalyst is different while example (2) represents homogeneous catalyst as both reactants and catalyst are in same state.

The role of a catalyst is highly specific to a particular reaction.

Example : $CO(g) + H_2(g) \rightarrow CH_4(g) + H_2O(g)$; Ni(s) is used as catalyst.

$CO(g) + H_2(g) \rightarrow HCHO(g)$; Cu (s) is used as catalyst.

A substance that catalyzes one reaction may have no effect on another reaction, even if that reaction is very similar. Many of the most highly specific catalysts are those designed by nature. The chemical reactions in living things are controlled by biochemical catalysts called enzymes.

Exercise 4.5

1. Explain what happens to the rate of reaction when temperature increases.
2. Define the term catalyst.
3. Explain the effect of surface area on the rate of reaction.
4. You are provided with a piece of zinc metal, dilute HCl (2M), zinc dust, ice-bath, test tube stand, water bath and Bunsen burner. Using the material provided, devise an activity to study the factors affecting reaction rate.

4.2. THEORIES OF REACTION RATES

At the end of this section, you should be able to:

- state collision theory;
- define activation energy;
- describe how collision theory can be used to explain changes in reaction rate;
- state the transition-state theory;
- define activated complex (transition state);
- describe how transition-state theory explains changes in reaction rate; and
- sketch and label the energy profiles of reactions that are exothermic and endothermic.

Two important theories help us to explain why different reactions occur at different rates. These are the collision theory and the transition-state theory. These two theories are distinct but in complete agreement, each emphasizing different aspects of reaction processes.

4.2.1. Collision Theory

Have you ever played billiards? Certain collisions result in scoring points while others are not fruitful enough as they lack in either power of impact or lack in angle placement.

Activity 4.4

Form a group and discuss each of the following questions;

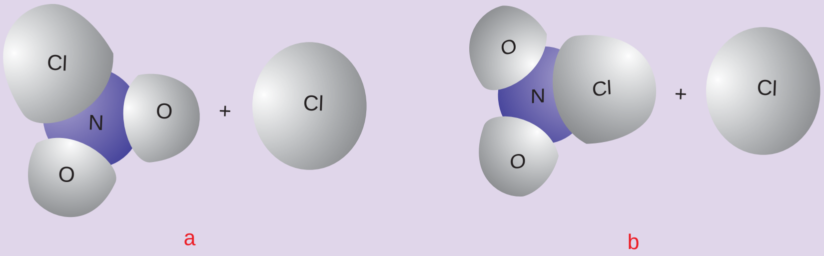
1. Ethanol can easily burn in air due to the following reaction.

$$CH_3CH_2OH + O_2 \rightarrow CO_2 + H_2O$$

In actual practice, you are required to use a lighter (igniter) to start the reaction. Why?

2. Consider the following reaction

$NO_2\,Cl + Cl \rightarrow NO_2 + Cl_2$



Which of the above collisions might be successful to form the product?

Share your ideas with the rest of the class.

Concentration and Collision Theory

The fundamental concept of the collision theory of rate of reaction is that, in order for a reaction to occur between reacting species (atoms, ions or molecules), they must first collide (come in contact). The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision).

$$\text{Rate } \alpha \ \frac{\text{number of collisions}}{\text{second}}$$

According to collision theory, the more collisions there are, the faster the rate of reaction would be. However, not all collisions between reacting species result in a reaction. This is because collisions between reactants can be either effective or ineffective. Effective collisions are collisions that result in a reaction to form the desired products. Ineffective collisions are collisions that do not result in a reaction to form the desired products.

In order for a collision between reactants to be effective, the reacting species must be in proper orientation to each other at the time of collision, they must collide with sufficient energy to break or rearrange bonds. The minimum energy required for a reaction to occur during a collision of reacting species is called the activation energy, E_a.

Postulates of collision theory are summarized below.

For a reaction to occur between reactants:

1. The particles of the reacting substances must collide.
2. The particles of the reacting species must have proper orientation.
3. The particles of the reactants must collide with energy greater than or equal to the energy of activation.

According to collision theory, only collisions with proper orientation of reacting species possessing sufficient energy result in a reaction. The collision can either be linear or non-linear (bent).

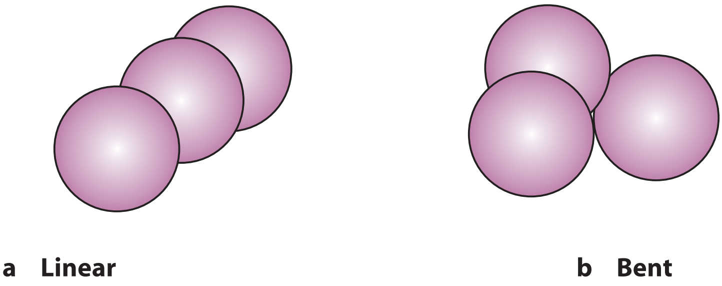


Figure 4.6 Orientation of molecules.

Generally, E_a for activated complex formed in linear orientation is less than that is formed in bent orientation. Hence, orientation (a) is favoured over orientation (b).

Concentration is one of the factors that influence the rate of reaction of a chemical reaction. Collision theory accounts for the observed increase in the rate of any reaction when the concentrations of reactants are increased. Increasing the concentrations of the reacting species results in higher number of collisions per unit time, and the reaction rate is correspondingly higher.

Temperature and Collision Theory

According to the kinetic molecular theory, the average kinetic energy of the particles of a substance is directly proportional to the absolute temperature. As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably. This causes the particles of the reactants to collide more frequently and with greater energy. This results in an increase in reaction rate.

4.2.2. Transition State Theory

Activity 4.5

Form a group and try to explore which among the following reactions absorb energy (endothermic) or release energy (exothermic):

a Burning of candle.

b Dissolution of ammonium chloride in water.

c Photosynthesis.

d Respiration.

Now discuss each of the following questions and, share your ideas with the rest of the class.

1. Prepare a table of two columns and two rows. In the first column, write exothermic reaction and in the second column, write endothermic reaction. In the second row, write one important way in which the two types of reactions differ.
2. Draw a potential energy diagram for each, (use the *x*-axis for the progress of the reaction (time), and the *y*-axis for potential energy).
3. Write two examples of endothermic and exothermic reactions.

Share your ideas with the rest of the class.

Transition-state theory was developed in 1935 simultaneously by Henry Eyring, Meredith Gwynne Evans and Michael Polanyi. It is also referred to as "activated-complex theory". According to transition-state theory, the collision between two reacting species results in the formation of an activated complex or transition state. An activated complex or transition state is a short-lived, high energy state species that is temporarily formed by the collision of reactant molecules before they form products.

These species can either form products or fall apart to give the original reactants. In the activated complex, the original bonds are lengthened and weakened, and the new bonds are only partially formed. Remember that chemical reactions involve the formation and breaking of chemircal bonds and are accompanied by changes in potential energy, which is related to bond energy. Let us consider the reaction:

$$A_2 + B_2 \rightarrow 2AB$$

where A_2 and B_2 are the reactants, and AB is a the product. Refer to Figure 4.7. As the reactants, A_2 and B_2, approach each other and collide, they begin climbing up the left side of the potential-energy hill, or barrier. If they have less energy than the energy of activation, E_a, they fail to climb the barrier and, instead, roll back down its left side. In this case, no reaction occurs.

If, however, they have energy that is at least equal to the energy of activation, they climb the barrier, roll down the other side, and convert to product.

In this concept, the level of activation energy required for a reaction is seen as the height of a barrier between the reactants and products. To convert from the reactant condition to the product condition, particles must climb the barrier.

The potential-energy curves in Figure 4.7 include representations of the barrier.

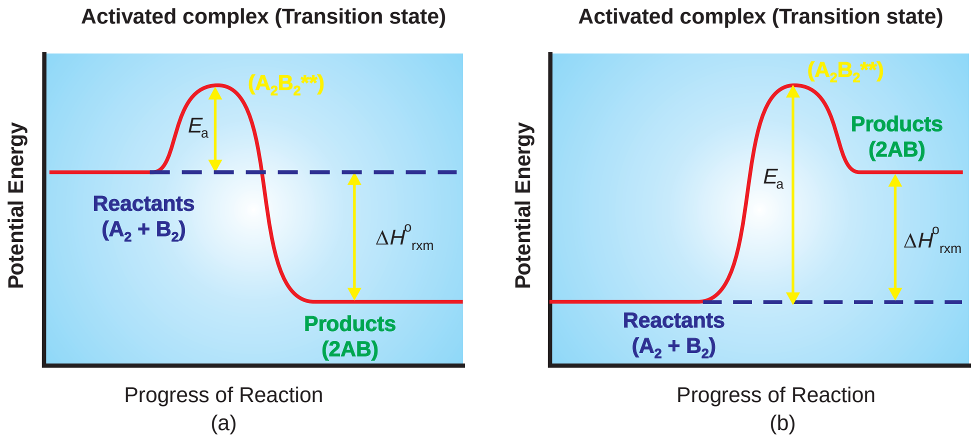


Figure 4.7 Reaction energy diagrams for a) exothermic and b) endothermic reactions.

The formation of an activated complex in the form of an equation can be shown as,

$$A_2 + B_2 \rightarrow A_2B_2^{\ddagger} \rightarrow 2AB$$

where $A_2B_2^{\ddagger}$ is the activated complex or transition state.

As shown in Figure 4.7, the activated complex corresponds to the peak of the energy barrier. According to transition-state theory, the rate of reaction depends on the rate at which reactants can climb to the top of the barrier and form an activated complex. On the other hand, the activation energy, E_a, is the energy that must be absorbed by the reactants to allow them to reach the transition state or the activated complex and cross the energy barrier.

For the exothermic reaction illustrated in Figure 4.7(a), the products have lower energy than the reactants and the standard reaction enthalpy is less than zero $\Delta H_r^o < O$.

In Figure 4.7(b), the thus energy of the products is higher than that of the reactants, thus for an endothermic reaction, $\Delta H^\circ_r > 0$.

Exercise 4.6

1. Define activation energy?
2. Describe transition-state theory.
3. How does a catalyst affect the rate of a reaction?
4. During a course of reaction , can only one activated complex be formed for a particular type of reaction?
5. Discuss the relationship between collision and rate of chemical reaction.

4.3 RATE EQUATION OR RATE LAW

At the end of this section, you should be able to:

- define rate law, order of reaction and rate constant;
- determine reaction order;
- calculate rate constants from given experimental data;
- describe the role of the rate constant in the theoretical determination of a reaction rate;
- explain the zero order, first order and second-order reactions, using concentration-versus- time curves;
- calculate that concentration and time the reaction mixture for different order reactions and plot their graphs; define half life;
- define half-life; and
- calculate the half lives of zero-order, first-order and second-order reactions from experimental data.

4.3.1 Order of Reaction and Rate Constant

Activity 4.6

You have studied that rate of a reaction increases with increase in concentration of reactants. Form a group and discuss each of the following questions and share your ideas with the rest of the class.

1. How many folds does the rate of reaction increases if concentration of a reactant is doubled?
2. Do all the reactants affect reaction rate in equivalent amount?
3. Does the reaction rate changes in the same ratio every time?
4. Why do you think chemists want to know the order of a reaction and the rate constant for a reaction?

The rate law or rate equation for a chemical reaction is an equation which links the reaction rate with the concentrations or pressures of reactants and certain constant parameters (*normally rate coefficients and partial reaction order*). To determine the rate equation for a particular system, one combines the reaction rate with a mass balance for the system.

For a simple reaction,

$$A \rightarrow B$$

Where A is reactant and B is the product. The rate law or rate equation for this reaction is written as:

$$\text{Rate} \propto [A]^x \quad \text{or} \quad \text{Rate} = k[A]^x \qquad \text{...(4.4)}$$

where [A] expresses the concentration of A (usually in moles per liter) and k is the rate constant of the reaction, and "x" is the order of the reaction. Note that "x" is not stoichiometric coefficient in the balanced equation and it is determined experimentally. The order of reaction is the power to which the reactant's concentration is raised in the rate law expression.

For reactions involving more than one reactant, the order of a reaction is the sum of the powers to which all concentrations are raised in the rate law expression. For the general reaction.

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

we can write the rate law expression as:

$$r = k[A]^x\ [B]^y \qquad ...(4.5)$$

The reaction is x^{th} order in A, y^{th} order in B, and $(x + y)^{th}$ order overall. Note that the order of a reaction is not necessarily the same as the stoichiometric coefficients in the balanced equation for the reaction. The value of the rate constant, k, depends on conditions such as temperature, concentration and surface area of the adsorbent or light irradiation.

Consider a reaction with the rate equation,

$$r = k[A]^2\ [B]$$

The reaction with the rate equation given above is described as "second-order in A" and "first-order in B." The overall reaction order is described as a third-order reaction overall, because the sum of the exponents on [A] and [B] is 3.

Some examples of the order of generalized rate equations for simple reactions are given in Table 4.2.

Table 4.2 Rate equation and reaction order for simple reaction rate

Rate equation	Overall reaction order
$k[A]^o$	zero
$k[A]$	first
$k[A]^2$	second
$k[A][B]$	second
$k[A]^3$	third
$k[A]^2[B]$	third
$k[A][B][C]$	third
$k[A]^{3/2}[B]$	5/2

Example 4.3

The rate equation for the oxidation of SO_2 to SO_3 in excess O_2 is:

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$$

$$\text{Rate} = k[SO_2]\ [SO_3]^{-½}$$

a What is the order of the reaction with respect to each substance in the rate equation?

b What happens to the rate of reaction as $[SO_3]$ increases?

Solution:

a The reaction is first-order with respect to SO_2, and is negative one-half order with respect to SO_3.

b As the concentration of SO_3 increases, the rate of reaction decreases.

To find the experimental rate equation by the method of initial rates, it is necessary to gather concentration-time data in a series of separate experiments. Each experiment must have a different initial concentration of one or more reactants. The experiments must be performed at the same temperature. The initial rate for each experiment can be found from the concentration-versus-time curve.

Suppose a reaction of the type,

$$A \longrightarrow \text{products}$$

is under study. The data are inspected to find how the initial rate varies with the initial concentration of A, $[A]_o$. The objective is to find the value of the exponent in the rate equation, $\text{rate} = k\,[A]^m$, where m is the order of the reaction. For a first-order reaction, $m = 1$, and the rate varies directly with $[A]_o$. If $[A]_o$ is doubled, the rate is doubled; if $[A]_o$ is tripled, the rate is tripled; and so on (see Table 4.3). For a second-order reaction, $m = 2$ and the rate is increased by a factor of 2^2, or 4, if $[A]_o$ is doubled, and so on. If the reaction is zero-order in A, changes in the concentration of A has no effect on the reaction rate. The order for each of several reactants can be found by varying one initial concentration at a time, while keeping the others constant.

Table 4.3 Change in initial rate with change in $[A]^o$ for rate = $k\,[A]^m$

For a reaction of	If $[A]^0$ is doubled	If $[A]^0$ is tripled
Zero-order (m = 0)	rate is unchanged	rate is unchanged
First-order (m = 1)	rate is doubled	rate is tripled
Second-order (m = 2)	rate is quadrupled (x 2^2)	rate is 9 times greater (x 3^2)

Example 4.4

The kinetics of the reaction,

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

was studied at 80 K by varying the initial pressures of the reactants individually and finding the initial reaction rates. The following data are typical of such a study.

Experiment	p_{init}(NO) (Torr)	$P_{init}(O_2)$ (Torr)	Rate of NO_2 formation (Torr/s)
a	1630	1630	6.13×10^{-8}
b	3260	1630	24.5×10^{-8}
c	1630	3260	12.2×10^{-8}

a What is the order of reaction with respect to each reactant?

b What is the value of the rate constant?

Solution:

a Order of reaction with respect to each reactant can be determined as follows. Holding the O_2 pressure constant, while doubling the NO pressure, quadrupled the rate, indicating that the reaction is second order in NO. With constant NO pressure, doubling the O_2 pressure caused the rate to double, showing that the reaction is first-order in O_2. The rate equation for the formation of NO_2 becomes

$$\text{Rate of } NO_2 \text{ formation} = kp^2_{NO}\, p_{O_2}$$

b The value of the rate constant. The experimental data can be used in the rate equation to find the value of *k*. For the data from experiment a, for example:

$$k = \frac{\text{Rate of } NO_2 \text{ formation}}{p^2_{NO}\, p_{O_2}}$$

$$\Rightarrow \quad k = \frac{6.13\times10^{-8}\ \text{Torr}/\text{s}}{(1630\ \text{Torr})^2 \times 1630\ \text{Torr}} = 1.42\times10^{-17}\ \text{Torr}^{-2}\text{s}^{-1}$$

The best value for *k* is taken as an average of the *k* values calculated for each run: in this case, it is 1.41×10^{-17} $\text{Torr}^{-2}\ \text{s}^{-1}$.

From experimental observations, in 1889, Svante Arrhenius, observed that a mathematical relationship connects activation energy, temperature, and the rate constant. This relationship is known as the Arrhenius equation and is written as:

$$k = Ae^{-Ea/RT} \qquad \text{...(4.6)}$$

where, k is a rate constant at temperature T, A is a constant, R is an ideal-gas constant, and E_a = activation energy.

Equation (4.6) shows the fraction of collisions in an elementary reaction in which the particles have enough energy to react. The constant A corrects for the frequency of collisions, the necessity for the proper orientation in effective collisions, and all factors other than activation energy that are significant in effective collisions.

Taking logarithms of both sides, the equation (4.6) becomes:

$$\log k = \left(\frac{-E_a}{2.303\,\mathrm{R}}\right)\frac{1}{T} + \log A \qquad \text{...(4.7)}$$

The above equations show that reactions with larger activation energies have smaller values of k and are, therefore, slower. The equation also shows that, for a given value of activation energy, as the temperature increases, the value of rate constant increases. This indicates that the reaction is faster, because at higher temperatures more molecules can collide effectively.

Equation (4.7) is the equation for a straight line. The value of E_a can be found from the slope of a plot of log k versus $1/T$, $E_a = -2.303\ R \times \text{slope}$. Also, by combining the equations for the values of k at two different temperatures T_1 and T_2 for the same reaction, a relationship is obtained that allows for the calculation of E_a:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \quad \log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \qquad \text{...(4.8)}$$

Alternatively, if E_a and three of the four values k_1, k_2, T_1, and T_2 are known, the fourth can be found. In using the Arrhenius equation, the energy is customarily expressed in joules, temperature must be in kelvin, and R is 8.314 J/ (K mol).

Example 4.5

The thermal decomposition of $CH_3N{=}NCH_3$ in the gas phase to give nitrogen and methyl radicals

$$CH_3N = NCH_3(g) \rightarrow N_2(g) + 2\ {\cdot}CH_3\ (g)$$

has an activation energy of 2.14×10^5 J/mol, at 600 K, at the given temperature, $k = 1.99 \times 10^8\ s^{-1}$. Does the reaction rate double with a ten-degree rise in temperature hold for this reaction?

Solution :

To answer the question, we must calculate k at 610 K, using the appropriate form of the Arrhenius equation. The knowns are E_a and k_1 at T_1 = 600 K, and T_2 = 610 K. The unknown is k_2 at 610 K.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\left(\frac{k_2}{1.99\times10^8 s^{-1}}\right) = \left(\frac{2.14\times10^5\ \text{J/mol}}{2.303\times8.314\ \text{J/(K mol)}}\right)\left(\frac{610\ \text{K} - 600\ \text{K}}{610\ \text{K}\times600\ \text{K}}\right)$$

Taking antilogarithms of both sides gives:

$$\frac{k_2}{1.99\times10^8\ s^{-1}} = 2.0$$

Therefore, $k_2 = (2.0)\ (1.99\ \times10^8\ s^{-1}) = 4.0\ \times\ 10^8\ s^{-1}$

Comparison of k_1 with k_2 shows that, for this reaction, the rate constant is doubled by a ten-degree rise in temperature. (This is not always the case.)

Exercise 4.7

1. Given that E_a for the hydrolysis of sucrose is 108×10^3 kJ / mol, compare the rate constant of this reaction at 37°C (T_1) with the rate constant of the same reaction at 27°C (T_2).
2. Calculate the rate constant for the above reaction at 47°C and compare it to the rate constant at 37°C.
3. Plot a graph of log k versus $1/T$ to calculate the activation energy.

4.3.2 Concentration-Time Equation (Integrated Rate Law)

Activity 4.7

Form a group and discuss each of the following questions.

1. How do you explain the concentration dependence of rate of reactions?
2. What is the mathematical expression for describing order of a reaction?
3. How do you distinguish between zero-order, first-order, and second-order reaction?

A rate law tells us how the rate of reaction depends on the concentration of the reactants at a particular moment. But, often we would like to have a mathematical relationship that shows how a reactant concentration changes over a period of time. A rate law can be transformed into a mathematical relationship between concentration and time using calculus. Therefore, an integrated law relates concentration to reaction time.

1. *Zero Order Reaction*

A zero-order reaction is a reaction whose rate of reaction does not depend on the reactant concentration. For the general reaction

$$\text{A} \longrightarrow \text{Product}$$

the zero order rate law is written as the equation

$$r = -\frac{\Delta[\text{A}]}{\Delta t} \quad \text{...(4.9)}$$

Using calculus, it can be shown from equation (4.9) that

$$[\text{A}]_t = -kt + [\text{A}]_o \quad \text{...(4.10)}$$

where $[\text{A}]$ is concentration of A at $t = t$; $[\text{A}]_o$ is the concentration of A is at $t = 0$. Now, zero-order reactions can be written as follows:

$$\boxed{[\text{A}]_t = -kt + [\text{A}]_o} \text{ ... Integrated rate equation for } 0^{th} \text{ order reaction} \quad \text{...(4.11)}$$

This is a linear equation with the form of $y = mx + b$. For a zero-order reaction, a plot of $[\text{A}]$ versus-time is a straight line, whose slope is $-k$.

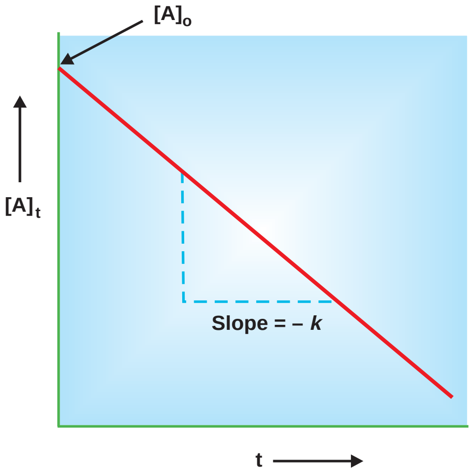


Figure 4.8 A plot of [A] versus t for a zero-order reaction.

Example 4.6

The decomposition of HI into hydrogen and iodine on a gold surface is zero-order in HI. The rate constant for the reaction is 0.050 Ms^{-1}. If you begin with a 0.500 M concentration of HI, what is the concentration of HI after 5 seconds?

Solution :

Use the integrated rate

$$[HI] = [HI]_0 - kt$$

The initial concentration is $[A]_0 = 0.500$ M, and the reaction runs for 5 seconds.

$$[HI] = 0.500\ M - 0.050\ M\ s^{-1} \times 5\ s = 0.250\ M$$

2. *First-Order Reactions*

A first-order reaction is a reaction whose rate of reaction depends on the reactant concentration raised to the first power. In a first-order of the type

$$A \longrightarrow \text{Product}$$

the rate is

$$r = \frac{\Delta[A]}{\Delta t} \qquad ...(4.12)$$

$$r = k\,[A] \qquad ...(4.13)$$

To obtain the units of k for this rate law, we write

$$k = \frac{r}{[A]} = \frac{M/s}{M} = 1/s \quad \text{or} \quad s^{-1}$$

Combining equations (4.12) and (4.13) for the rate, we get

$$-\frac{\Delta[A]}{\Delta t} = k[A] \qquad \text{...(4.14)}$$

Using calculus, it can be shown from equation (4.14) that

$$\ln \frac{[A]_t}{[A]_o} = -\, kt \qquad \text{...(4.15)}$$

where ln is the natural logarithm, and $[A]_o$ and $[A]$ are the concentrations of A at times $t = 0$ and $t = t$, respectively. It should be understood that $t = 0$ need not correspond to the beginning of the experiment. It can be any time at which we choose to start monitoring the change in the concentration of A,

Equation (4.15) can be rearranged as follows:

$\boxed{\ln [A]_t = -\, kt + \ln [A]_o}$ ... Integrated rate equation for 1st order reaction: ...(4.16)

Equation (4.16) has the form of the linear equation $y = mx + b$, in which m is the slope of the line that is the graph of the equation. Thus, a plot of ln $[A]$ versus t gives a straight line with a slope of k (or m). This graphical analysis allows us to calculate the rate constant k. Figure 4.9 shows the characteristics of first-order reactions.

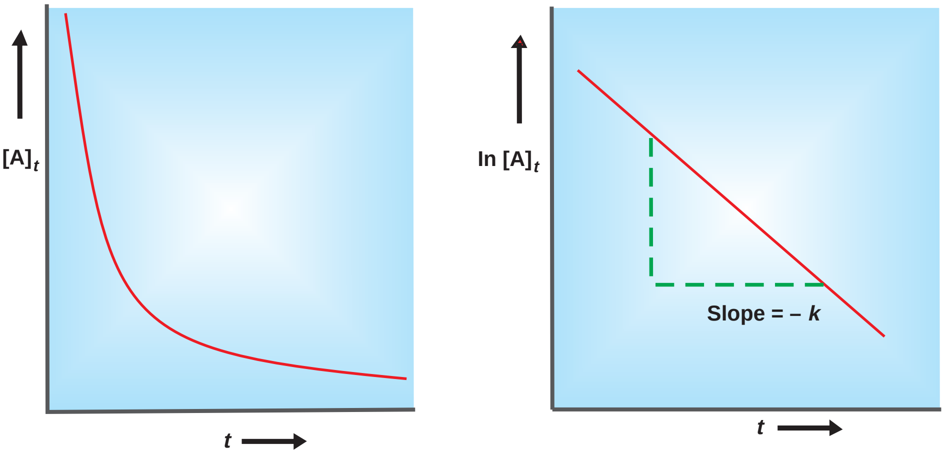


Figure 4.9 Plot for a reaction that is first-order with respect to A, first-order overall.

Note! The observation that plot of ln[A] versus time is a straight line confirms that the reaction is first-order in A and first-order overall, *i.e.*, Rate = k[A]. The slope is equal to $-k$.

In the following example, we apply equation (4.16) to a reaction.

Example 4.7

The conversion of cyclopropane in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4}\ s^{-1}$ at 500°C.

$$\underset{\text{cyclopropane}}{C_3H_6} \quad \rightarrow \quad \underset{\text{propene}}{CH_3 - CH = CH_2}$$

a If the initial concentration of cyclopropane is 0.25 M, what is the concentration after 8.8 minutes?

b How long does it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M?

c How long does it take to convert 74 % of the starting material?

Solution :

a Applying equation (4.16),

$$\ln \frac{[A]_o}{[A]} = kt$$

Solving the equation, we obtain

$$\ln \frac{0.25\,M}{[A]} = 0.354$$

$$\frac{0.25\,M}{[A]} = e^{0.354} = 1.42$$

$$[A] = 0.18\ M$$

b Again using equation (4.16), we have

$$\ln \frac{0.25\ M}{0.15\ M} = (6.7\times10^{-4}s^{-}) \ t$$

$$t = 7.6\times10^{2}\ \text{s}$$

$$= 13\ \text{minutes}$$

c In a calculation of this type, we do not need to know the actual concentration of the starting material. If 74% of the starting material has reacted, the amount left after time t is (100% – 74%), or 26%. Thus, $[A]/[A]_o = 26/100 = 0.26$. From equation (13.3), we write

$$t = \frac{1}{k}\ln\frac{[A]_o}{[A]}$$

$$= \frac{1}{6.7\times10^{-4}\text{s}^{-1}}\ln\frac{1.0\ \text{M}}{0.26\ \text{M}}$$

$$= 2.0\times10^{3}\ \text{s}$$

$$= 33\ \text{minutes}$$

3. *Second-Order Reactions*

A second order reaction is a reaction whose rate depends either on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power. The simpler type of reaction involves one kind of reactant molecule

$$aA \longrightarrow \text{Product}$$

where

$$r = -\frac{\Delta[A]}{\Delta t} \qquad \text{...(4.17)}$$

From the rate law

$$r = k[A]^{a} \qquad \text{...(4.18)}$$

As before, we can determine the units of k by writing

$$k = \frac{r}{[A]^{a}} = \frac{\text{M/s}}{\text{M}^{2}} = \text{M}^{-}\text{s}^{-} \qquad \text{...(4.19)}$$

For simplicity, we will consider a second order reaction with a rate law of the following type:

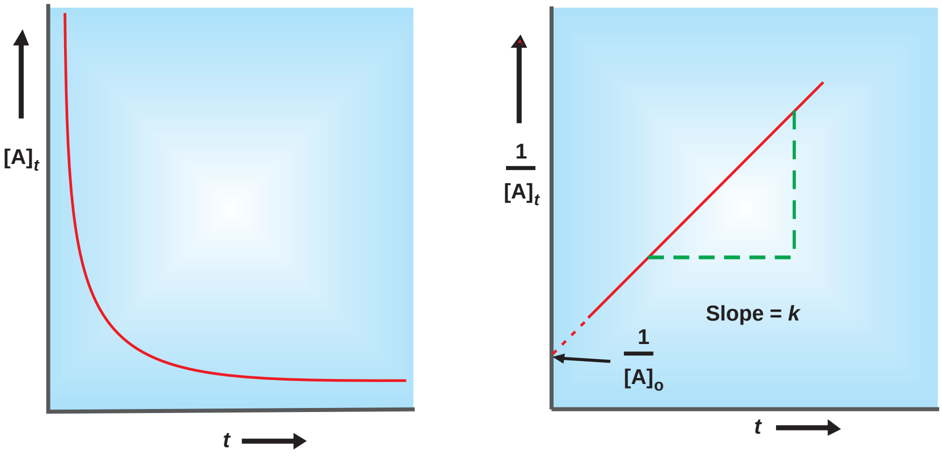
$$2A \longrightarrow \text{product}$$

$$r = k[A]^2$$

By using calculus, use can obtain the expression

$$\boxed{\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}} \quad \text{... Integrated rate equation for 2}^{\text{nd}}\text{ order reaction} \quad \text{...(4.20)}$$

The graph of $\frac{1}{[A]}$ versus time gives a straight line with a slope of k as shown in Figure 4.10.



(a) *(b)*

Figure 4.10 Plots for a reaction that is second-order with respect to A and overall a second-order reaction.

Another type of second-order reaction is

$$A + B \longrightarrow \text{product}$$

and the rate equation is given by

$$r = k[A][B] \qquad \text{...(4.21)}$$

where the reaction is first-order in A and first-order in B. Thus, this reaction has an overall reaction order of 2.

The corresponding integrated rate equation for such type of second order-reaction is too complex for our discussion and beyond the scope of this text book.

Example 4.8

Nitrosyl chloride, NOCl, decomposes slowly to NO and Cl_2 as shown in the equation below.

$$2NOCl \longrightarrow 2NO + Cl_2$$

$$r = k[NOCl]^2$$

The rate constant, k equals 0.020 L mol^{-1} s^{-1} at a certain temperature. If the initial concentration 0.050 M, what will the concentration be after 30 minutes?

Solution:

$[NOCl] = 0.050\ M$ $\qquad k = 0.020\ L\ mol^{-1}\ s^{-1}$

$[NOCl]_t = ?\ M$ $\qquad t = 30\ min = 1800\ s$

The integrated rate equation for this reaction is given by:

$$\frac{1}{[NOCl]_t} = kt + \frac{1}{[NOCl]_o}$$

$$= (0.020\ L\ mol^{-1}\ s^{-1})\ (1800\ s) + \frac{1}{0.50\ mol^{-1}}$$

$$= 50\ L\ mol^{-1}$$

$$\therefore\ [NOCl]_t = 0.018\ L\ mol^{-1} = 0.018\ M$$

4.3.3 The Half-life of a Reaction

Activity 4.8

Form a group and do as directed:

1. Plot a graph that shows the time dependence of concentration of reactant for the 1st order reaction.
2. On the graph show the time when the concentration of a reactant is decreased by half of its initial amount. What do you call this situation?

Discuss the results and share your ideas with the rest of the class.

The half life of a reaction is defined as the time required for the concentration of a reactant to decrease to half of its initial concentration. This means that half-life is the time it takes for the concentration of A to fall from $[A]_o$ to $½[A]_o$, *i.e* $[A] = ½[A]_o$. The half-life of a reaction is designated by the symbol, $t_{½}$.

The mathematical expression for the half-life of a first-order reaction is determined by substituting $t = t_{½}$ and $[A] = ½[A]_o$ in equation

$$\log \frac{[A]_o}{[A]_t} = \frac{kt}{2.303}$$

This gives us

$$\ln \frac{[A]_o}{½[A]_o} = \frac{kt_{½}}{2.303} \quad \text{or} \quad \ln 2 = kt_{½} \qquad ...(4.23)$$

And solving for $t_{½}$ gives, $\frac{\ln 2}{k} = \frac{0.693}{k}$.

From the relation, it can be noted that, for a first-order reaction, the half-life is independent of the initial concentration of A, $[A]_o$.

For second-order reactions, half-life depends on the initial concentration, $[A]_o$, and the rate constant, k. For a second-order reaction, the half-life expression is given by the equation

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt \Rightarrow \frac{1}{½[A]_o} - \frac{1}{[A]_o} = kt_{½} \qquad ...(4.24)$$

Rearranging and solving for $t_{½}$, we get the expression,

$$t_{½} = \frac{1}{k[A]_o} \qquad ...(4.25)$$

Summary of equations for 1st and 2nd order reactions is given in Table 4.4.

Table 4.4 Summary of the kinetics of first-order and second order reactions

Order	Rate equation	Concentration-time equations	Half-life
1st	rate = $k[A]$	$\ln\frac{[A]_o}{[A]} = kt$	$\frac{0.693}{k}$
2nd	rate = $k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_o} + kt$	$\frac{1}{k[A]_o}$

Example 4.9

The decomposition of N_2O_5 in CCl_4 at 45 °C is first order reaction with $k = 6.32 \times 10^{-4}\ s^{-1}$. If the initial concentration of N_2O_5, is 0.40 mol/L:

a Calculate $t_{½}$.

b Find the concentration of N_2O_5 remaining after $t_{½}$.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

Solution:

a $$t_{½} = \frac{0.693}{k} = \frac{0.693}{6.32 \times 10^{-4} s^{-1}} = 1097 \text{ s}$$

b The equation relating time and concentration for a first-order reaction is used with $[N_2O_5]_o$ = 0.40 mol/L and t = 1097 s to find $[N_2O_5]$.

$$\ln[N_2O_5] = -kt + \ln[N_2O_5]_o$$

$$= (-6.32 \times 10^{-4} \text{ s}^{-1})(1097 \text{ s}) + \ln(0.40)$$

$$= (-0.693) + (-0.9163) = -1.6096$$

Taking the inverse of the natural logarithms of both sides gives the concentration of N_2O_5 remaining after 1.0 hour,

$$[N_2O_5] = 0.1996 \text{ mol/L} \cong 0.20 \text{ mol/L}.$$

Exercise 4.8

1. If a certain first-order reaction has a half-life of 30.0 minutes,
   a Calculate the rate constant for this reaction.
   b How much time is required for this reaction to be 35% complete?
2. The rate constant for the formation of hydrogen iodide from the elements,

   $$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

   is 2.7 × 10^{-4} L/(mol.s) at 600 K and 3.5 × 10^{-3} L/(mol.s) at 650 K.
   a Find the activation energy E_a.
   b Calculate the rate constant at 700 K.
3. The rate constant for the decomposition of N_2O_5 in chloroform,

   $$2N_2O_5 \xrightarrow{CHCl_3} 4NO_2 + ½O_2$$

   was measured at two different temperatures, T_1 = 25 °C, $k_1 = 5.54 \times 10^{-5}$ s^{-1} and T_2 = 67 °C, $k_2 = 9.30 \times 10^{-3}$ s^{-1}. Find the activation energy for this reaction.

4.4 REACTION MECHANISM

At the end of this section, you should be able to:

- explain reaction mechanism;
- explain the molecularity of a reaction;
- explain what is meant by rate determining step;
- give specific examples to illustrate rate determining step;
- explain the relationship between the reaction path way and the rate law; and
- use rate equation to suggest possible reaction mechanism for a reaction.

An overall balanced chemical equation does not give any information about how a reaction actually takes place. In many cases, it merely represents the sum of several elementary steps, or elementary reactions, a series of simple reactions that represents the progress of the overall reaction at the molecular level. The term for the sequence of elementary steps that leads to product formation is reaction mechanism. The reaction mechanism is comparable to the simplest description you might give of the route of a trip you plan to take. The overall chemical equation specifies only the origin and destination, while the reaction mectanim describes the stopovers also.

As an example of a reaction mechanism, let us consider the reaction between nitric oxide and oxygen:

$$2NO(g) \ + \ O_2(g) \ \rightarrow \ 2NO_2(g)$$

We know that the products are not formed directly from the collision of two NO molecules with an O_2 molecule, because N_2O_2 is detected during the course of the reaction. Let us assume that the reaction actually takes place via two elementary steps as follows:

$$2NO(g) \ \rightarrow \ N_2O_2(g)$$

$$N_2O_2(g) \ + \ O_2(g) \ \rightarrow \ 2NO_2(g)$$

In the first elementary step, two NO molecules collide to form a N_2O_2 molecule. This event is followed by the reaction between N_2O_2 and O_2 to give two molecules of NO_2. The net chemical equation, which represents the overall change, is given by the sum of the elementary steps:

Elementary step: $NO + NO \rightarrow N_2O_2$

Elementary step: $N_2O_2 + O_2 \rightarrow 2NO_2$

Overall reaction $2NO + O_2 \rightarrow 2NO_2$

Species such as N_2O_2 are called intermediates because they appear in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation.

4.4.1 Molecularity of an Elementary Reaction

Activity 4.9

Form a group and try to identify the number of molecular species involved in each of the following reactions:

1. $A \rightarrow$ products
2. $A + A \rightarrow$ products
3. $A + B \rightarrow$ products
4. $A + A + B \rightarrow$ products
5. $A + B + C \rightarrow$ products.

Share your findings with the rest of the class.

The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of a reaction. It is the number of reactant molecules taking part in a single step of the reaction.

Example 4.10

a $PCl_5 \rightarrow PCl_3 + Cl_2$ (Unimolecular)

b $2HI \rightarrow H_2 + I_2$ (Bimolecular)

c $2SO_2 + O_2 \rightarrow 2SO_3$ (Termolecular)

d $NO + O_3 \rightarrow NO_2 + O_2$ (Bimolecular)

e $2CO + O_2 \rightarrow 2CO_2$ (Termolecular)

f $2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$ (Termolecular)

In the reaction that involve sequence of steps rate is determined by the flowest step.

Example 4.11

Decomposition of H_2O_2 takes place in the following two steps:

Step 1: $H_2O_2 \rightarrow H_2O + [O]$ (Slow)

Step 2: $[O] + [O] \rightarrow O_2$ (fast)

$H_2O_2 \rightarrow H_2O + 1/2O_2$ (overall reaction)

The slowest step is rate-determining. Thus, from step 1, reaction appears to be unimolecular.

It may be noted that molecularity is a theoretical concept and it cannot be zero, negative, fractional, infinite and imaginary.

Exercise 4.9

1. Give the meanings of each of the following terms:
   - a Elementary steps
   - b Unimolecular reaction
   - c Bimolecular reaction
   - d Termolecular reaction
2. Determine the molecularity of the following reactions:
   - a $NH_4NO_2 \longrightarrow N_2 + 2H_2O$
   - b $O_3 + NO \longrightarrow NO_2 + O_2$
   - c $2NO + O_2 \longrightarrow 2NO_2$

4.4.2 Rate-Determining Step

Activity 4.10

Form a group and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. What do you think a rate determining step is?
2. Why do chemists want to know the rate determining step?

In a multi-step reaction, all the elementary reactions do not necessarily proceed at equal rates. One of them might be very rapid, moderate or very slow. The reactants can be converted to products only as fast as they can complete the slowest step. The slowest step in the sequence of steps leading to the formation of products is called the rate-determining step. In other words, the slowest step in the mechanism determines the overall rate of the reaction.

Because the rate-determining step limits the rate of the overall reaction, its rate law represents the rate law for the overall reaction. For example, the reaction of NO_2 with F_2 is given by the equation:

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

The experimentally determined rate law is: Rate = $k[NO_2][F_2]$, the proposed reaction mechanism is:

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + \cdot F \qquad \text{slow}$$

$$NO_2 + \cdot F \xrightarrow{k_2} NO_2F \qquad \text{fast}$$

Let us check whether the proposed mechanism agrees with the experimental rate law or not. First, the sum of these reaction steps must give the overall balanced equation:

$$\begin{array}{lrcl} & NO_2 + F_2 & \rightarrow & NO_2F + \cdot F \\ & NO_2 + \cdot F & \rightarrow & NO_2F \\ \hline \text{Overall equation:} & 2NO_2 + F_2 & \rightarrow & 2NO_2F \end{array}$$

So, the first requirement is satisfied. The formation of $\cdot F$ in the first step occurs more slowly than its reaction with NO_2 to form NO_2F in the second step. Thus, the rate of formation of NO_2F in the second step is controlled by the rate of formation of $\cdot F$ in the first step. The overall rate cannot be faster than that of the slowest step.

Overall rate = the rate of the slowest step

The rate law agrees with experimentally determined rate law. So, the proposed mechanism is acceptable because it satisfies both requirements.

Exercise 4.10

Answer each of the following questions.

1. Describe the term molecularity of a reaction.
2. How do you identify the rate determining step for a reaction that involves more than one step?
3. The reaction

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

can be thought of as occurring in two elementary steps:

a $NO_2 + NO_2 \rightarrow NO + NO_3$ (slow step)

b $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast step)

Identify the rate determining step and determine the molecularity of this reaction.

Unit Summary

- *Chemical kinetics is the study of the rates and mechanisms of chemical reactions.*
- *A chemical reaction occurs when atoms, molecules or ions undergo effective collisions.*
- *The larger the activation energy, the slower a chemical reaction and vice versa.*
- *In general, reaction rates increase with temperature, because higher temperature increases both the frequency of collisions and the number of molecules possessing enough energy to undergo effective collision.*
- *A chemical equation represents an elementary reaction only if the reaction in the equation represents the actual atoms, molecules or ions that must interact for the reaction to occur.*
- *Elementary reactions that are bimolecular (the most common) have two*

reactant species, while unimolecular reactions have only one and termolecular reactions have three.

- *Reaction rate is expressed as the change in concentration of a reactant or product, per unit time.*
- *Both reaction rates and rate equations must be determined experimentally, often by gathering data on the variation of concentration over time.*
- *Rate equations often take the form of*

  $Rate = k[A]^m[B]^n[C]^p$

  where the sum of m, n, p, is the overall reaction order. The order of a specific reactant is given by m, or n, or p, and the exponents in a rate equation are often 1,2 or 3, but may also be fractions or negative numbers.
- *Rates of first-order and second-order reactions are dependent upon the concentrations of one or two reactants, respectively. In contrast, rates of zero-order reactions are independent of reactant concentrations.*
- *The half-life of a first order reaction is independent of the initial reactant concentration, whereas half-life of second order reaction depends on the initial reactant concentration.*
- *Reaction rates are influenced by the concentrations of reactants, temperature, catalysts and the degree of contact between reactants (surface area).*
- *Reaction rates and rate constants vary with temperature.*
- *The Arrhenius equation gives the relationships among the temperature, the rate constant and the activation energy for a given reaction, either for an elementary reaction or an overall reaction.*
- *In a heterogeneous reaction, the reactants are in different phases and the rates of such reactions are limited by the amount of the contact between reactants.*
- *Catalysts increase the rates of chemical reactions but can be recovered unchanged at the end of a reaction.*

Check List

Key terms of the unit

- *Average rate*
- *Bimolecular*
- *Catalyst*
- *Collision theory*
- *Concentration-time equation*
- *Elementary reaction*
- *Energy profiles of exothermic and endothermic reactions*
- *Half-life of a reaction*
- *Instantaneous rate*
- *Molecularity*
- *Order of reaction*
- *Rate constant*
- *Rate equation or rate law*
- *Rate of reaction*
- *Rate-determining step*
- *Reaction mechanism*
- *Surface area*
- *Termolecular*
- *Transition-state theory*
- *Unimolecular*

REVIEW EXERCISE

Part I: Multiple Choices

1. The rate constant for the decomposition of gaseous CH_3CHF_2

$$CH_3CHF_2(g) \rightarrow CH_2CHF(g) + HF(g)$$

is 7.9×10^{-7} s^{-1} at 429°C and 1.7×10^{-4} s^{-1} at 522°C. The activation energy for this reaction is:

a 340×10^{-5} s^{-1}

b 270 kJ mol^{-1}

c 135 kJ mol^{-1}

d None

2. Which of the following is not the concern of chemical kinetics?

a study of "how fast?" a chemical reaction goes to completion.

b study of the individual steps in a chemical reaction.

c study of "how far?" a chemical reaction goes to completion.

d none of the above.

3. The short-lived combination of reacting atoms, molecules, or ions that is intermediate between reactants and products is:

   a transition state
   c intermediate
   b activated complex
   d B and C
   e A and B

4. Which of the following is false about activation energy, E_a?

   a It is the minimum energy that reactants must have for a reaction to occur.
   b It is the difference in energy between the transition state and the reactants.
   c It is always negative.
   d None of the above.

5. The correct expression for a second-order reaction is

   a rate = $2k[A]$
   c rate = $k[A][B]$
   b rate = $k[A]^2$
   d both b and c

6. Which of the following is true about the factors influencing rate of reaction?

   a As surface area of reactants decreases, the rate of a reaction decreases.
   b As concentration of a reactant increases, the rate of the reaction increases except for zero-order reactions.
   c As temperature increases, the rate of reaction decreases.
   d A catalyst always speeds up the rate of a reaction.

7. Which of the following does not affect the rate of chemical reactions?

   a temperature
   c catalyst
   b concentration
   d none

8. According to the transition state theory, reactants must ____ in order to form product(s).

   a collide
   b go over an energy barrier
   c have lower free energy than the products
   d be catalyzed

9. The rate of a chemical reaction, that is independent of concentration is:

a	2nd order	c	0th order
b	1st order	d	None

10. Formation of an activated complex is explained by:

a	molecular kinetic theory	c	transition-state theory
b	valence-bond theory	d	collision theory

11. Consider the following reaction mechanism:

First step: $N_2O_5 \rightarrow NO_2 + NO_3$ (fast)

Second step: $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ (slow)

Third step: $NO_3 + NO \rightarrow NO_2$ (fast)

Which step is the rate-determining step?

a	First step	c	Third step
b	Second step	d	All of these

12. Which of the following statements is correct?

a Reactions with high activation energies are fast.

b Collisions between reactant particles with insufficient energies succeed in forming products.

c A catalyst can decrease the rate of a chemical reaction by changing the pathway of activation energy.

d All of the above.

13. Which of the following is false?

a The smaller the activation energy, the slower a reaction tends to be.

b In general, reaction rates increase with increase in temperature.

c The heat of reaction is the difference between the energy of the products and the energy of the reactants.

d All of the above.

14. A typical pathway for a chemical reaction that includes several simple steps is:

a	elementary reactions	c	an intermediate reaction
b	activation energy	d	none of the above

15. Which pair is the correct reaction rate expression for the following reaction?

$$2O_3(g) \rightarrow 3O_2(g)$$

a $-\frac{1}{2}\frac{\Delta[O]_3}{\Delta t}$ and $\frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$

c $\frac{1}{2}\frac{\Delta[O_3]}{\Delta t}$ and $-\frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$

b $-\frac{1}{2}\frac{\Delta[O_3]}{\Delta t}$ and $-\frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$

d $-\frac{1}{3}\frac{\Delta[O_3]}{\Delta t}$ and $\frac{1}{2}\frac{\Delta[O_2]}{\Delta t}$

16. The greatest increase in the rate for the reaction between X and Z with rate $r = k[X][Z]^2$ will be caused by:

a doubling the concentration of Z

b doubling the concentration of X

c tripling the concentration of X

d lowering the temperature

17. The oxidation of iodide ions by hypochlorite ions occurs by a three-step mechanism in an aqueous solution.

Step 1: $OCl^- + H_2O \rightarrow HOCl + OH^-$

Step 2: $I^- + HOCl \rightarrow HOI + Cl^-$

Step 3: $HOI + OH^- \rightarrow IO^- + H_2O$

The intermediate species in this reaction is/are:

a HOCl

c OH^-

b HOI

d all of the above

18. The reaction of nitric oxide with hydrogen at 1000 K is:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The rate of disappearance of NO is:

$$r = \frac{-\Delta[NO]}{\Delta t} = 5.0 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}.$$

What is the rate of formation of N_2?

a 2.5×10^{-5} mol L^{-1} s^{-1}

c 1.5×10^{-4} mol L^{-1} s^{-1}

b 5.0×10^{-5} mol $L^{-1}s^{-1}$

d 1.0×10^{-4} mol L^{-1} s^{-1}

19. A first-order reaction, $B \rightarrow P$, has a half-life of 100 s, whatever the quantity of substance B involved in a particular reaction. Which of the following is true?

    a The reaction goes to completion in 200 s

    b The quantity remaining after 200 s is half of what remains after 100 s.

    c 100 s is required for the reaction to begin.

    d Nothing can be said about the reaction.

20. Which of the following is true?

    a Rate depends on the manner in which molecules collide with each other.

    b Rate is inversely proportional to frequency of collision.

    c As a very rough approximation, we find a 10°C temperature increase, decreases the rate by half.

    d None.

21. The rate at a given specific time is:

    a average rate
    c rate of a reaction
    b instantaneous rate
    d formal rate

22. If we double the concentration of a reactant, the rate increase by four times, the reaction is:

    a second-order
    c first-order
    b zero-order
    d none

23. Substances that slow down a reaction are:

    a Promoters
    c inhibitors
    b Positive catalysts
    d none

Part II: Answer the following questions briefly

24. For the reaction between gaseous chlorine and nitric oxide,

$$2NO + Cl_2 \rightarrow 2NOCl$$

it is found that doubling the concentration of both reactants increases the rate by a factor of eight, but doubling the chlorine concentration only doubles the rate.

a What is the order of the reaction with respect to NO?

b What is the order of the reaction with respect to Cl_2?

c What is the overall order of the reaction?

25. Distinguish between the order and the molecularity of a reaction.

26. Explain the differences between endothermic and exothermic reactions.

27. What are pseudo unimolecular reactions? Write an example of such a reaction.

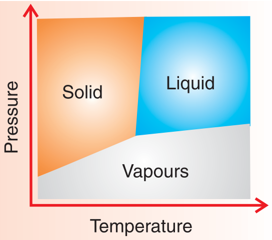
28. What are clock reactions?

29. The concentration of A during a reaction of the type: $A + 2B \rightarrow \text{products}$, changes according to the data in the table.

Time/min	**[A]/mol dm–3**
1	0.317
5	0.229
10	0.169
15	0.130
25	0.091
40	0.062

Based on the information given in the above table, calculate the average rate of reaction and plot a graph of rate of reaction versus time.

UNIT 5



Chemical Equilibrium and Phase Equilibrium

Unit Outcomes

At the end of this unit, you should be able to:

- *understand how equilibrium is established;*
- *explain characteristics of dynamic equilibrium;*
- *state the law of mass action, and write an expression for equilibrium constants, K_c and K_p, from a given chemical reaction;*
- *apply the law of mass action to calculate K_c,and K_p, the concentration and pressure of substances in equilibrium;*
- *understand how the reaction quotient is used to indicate the position of equilibrium;*
- *state Le Chateliers' principle and use it to predict and explain the effects of changes in temperature, pressure, concentration and presence of catalyst on a reaction;*
- *perform an activity to demonstrate the effects of changes in concentration on the position of equilibrium and to determine K_c and K_p values;*
- *explain how equilibrium principles are applied to optimize the production of industrial chemicals (e.g. the production of ammonia and sulphuric acid); and*
- *demonstrate scientific enquiry skills, observing, predicting, comparing and contrasting, communicating, asking questions and making generalizations.*

MAIN CONTENTS

Start-up Activity

Form a group and perform the following activity:

1. Mix 10 mL of 0.1 mol L^{-1} HCl solution with 10 mL of 0.1 mol L^{-1} NaOH solution. Now, discuss each of the following questions:
   a What is the concentration of NaCl formed?
   b How much HCl and NaOH remain unreacted?
   c Is the reaction complete?

2. Can you predict how much ammonia will be formed when 0.1 mol of nitrogen gas and 0.3 mol of hydrogen gas are allowed to react in a closed 2-litre flask? Share your ideas with the rest of the class.

INTRODUCTION

In the unit on chemical kinetics you have studied about one aspect of a chemical reaction, which is the rate of the reaction. You have also studied the time taken for half the reaction to be over. However, some questions such as the following still remain. Do all reactions reach completion? If not then how much of the reactants remain unreacted, that is, what is the extent of the reaction? Why does the reaction not reach completion? Why does it attain equilibrium? These questions can be answered after studying chemical equilibrium.

In this unit, you will study about equilibrium, how it is attained, different phases in which a system can exist and stability of these phases under different conditions of temperature and pressure.

5.1 CHEMICAL EQUILIBRIUM

At the end of this section, you should be able to:

- explain reversible and irreversible reactions;
- define dynamic chemical equilibrium;
- state the necessary conditions for the attainment of equilibrium;
- describe the microscopic events that occur when a chemical system is in equilibrium;
- describe characteristics of chemical equilibrium;
- state the law of mass action;
- define equilibrium constant;
- write the equilibrium constant expression for chemical reactions that involve concentration and partial pressure;
- calculate values for equilibrium constants involving concentration and partial pressure;
- state the relationship of K_{eq} to relative amounts of product and reactants in a given reaction;

- show the relationship between K_c and K_p;
- distinguish between homogeneous and heterogeneous reactions;
- define reaction quotient;
- use the equilibrium quotient to predict the direction of a reaction and the position of equilibrium;
- calculate equilibrium concentrations, given initial concentrations;
- determine whether the reactants or the products are favoured in a chemical reaction, given the equilibrium constants;
- list factors that affect chemical equilibrium;
- state Le-Chatelier's principle;
- use Le-Chatelier's principle to explain the effect of changes in temperature, pressure/volume, concentration and presence of a catalyst on a reaction;
- describe the effects of changes in concentration, pressure/volume and temperature on K_{eq};
- perform an activity to demonstrate the effects of changes in concentration and temperature on the position of equilibrium;
- perform an activity to determine K_c for esterification of organic acids;
- define optimum condition; and
- explain how Le-Chatelier's principle is applied to the Haber process for manufacturing ammonia and to the contact process for manufacturing sulphuric acid.

5.1.1 Reversible and Irreversible Reactions

Activity 5.1

Form a group and perform the following activity:

In a test tube take crushed ice. Dip a thermometer in it and note the temperature. Heat it slowly for a few seconds.

Now stop heating and place the test tube in a beaker containing large amount of crushed ice. Discuss the following questions in your group:

1. What is the temperature of crushed ice?
2. What happens when it is heated slightly?
3. What happens when it is cooled again?
4. What is the final temperature?

Share your ideas with the rest of the class.

A reversible reaction is a chemical reaction that results in an equilibrium mixture of reactants and products; for example, formation of ammonia is a reversible reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Another example of reversible reaction is the formation of hydrogen iodide from hydrogen gas and iodine vapours.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Activity 5.2

Form a group and perform the following activity:

1. Take 10 mL of 0.1 M HCl solution in a test tube and dip the corner of blue and red litmus papers respectively in it. What happens?
2. In another test tube take 10 mL of 0.1 M NaOH solution and dip the corner of blue and red litmus papers respectively in it. What happens?
3. Mix the above two solutions and again test with litmus papers.
4. Dissolve a few crystals of sodium chloride in 10 mL water and test it with blue and red litmus papers. Will the resulting solution be acidic or basic? Compare the results of 3 and 4.

Share your findings with rest of the class.

Chemical reactions which proceed in only one direction are known as irreversible reactions. When the equation for irreversible reaction is written, a single arrow (→) is used indicating that the reaction can proceed in only one direction.

While writing reversible reaction, double arrow ($\rightleftharpoons$) is used indicating that the reaction can go from reactant to product side and also from the product to the reactant side. The reaction from the reactant side to the product side is known as forward reaction and reaction from product to the reactants is known as reverse or backward reaction.

Exercise 5.1

Answer the following questions:

1. Define the terms reversible reaction and irreversible reaction.
2. Give examples of reversible and irreversible reactions.
3. Which symbol or sign is used to represent the reversibility and irreversibility of the reaction?

5.1.2 Attainment and Characteristics of Chemical Equilibrium

Equilibrium

Activity 5.3

Form a group and perform the following activity:

Take 10 mL of acetone in a test tube. Close the mouth of the test tube immediately. Clamp the test tube vertically. Mark the level of acetone with the marker. Allow it to stand for half an hour and note the level of acetone at regular intervals.

Discuss the findings with the class.

The equilibrium is *dynamic* in nature which means that although at the macroscopic level the properties do not change with time, however, at the molecular level the two processes are still taking place. So the equilibrium is attained when the rate of two opposing processes become equal.

Ice and water present together in a thermos flask at 0°C is another example of dynamic equilibrium. The equilibrium is attained when the rates of melting and freezing become equal.

The saturated solution is also an example of dynamic equilibrium. Saturated solution is a solution in which undissolved solute is in equilibrium with the solute dissolved in the solution. The molecules from undissolved solute go into the solution and equal number of solute molecules get precipitated from the solution. Therefore, the concentration of the solution remains constant.

Chemical Equilibrium

An equilibrium involving a chemical reaction is known as chemical equilibrium. When a chemical reaction takes place, the reactants are consumed and the products are formed. As a result the concentrations of reactants decrease with time and that of products increase. If the reaction is reversible in nature and it takes place in a closed vessel then the products decompose to give back reactants. After some time the concentrations of the reactants and products become constant, that is they do not change with time. This state is known as chemical equilibrium.

Chemical equilibrium is the state of the reaction when the macroscopic properties like temperature, pressure, volume and concentration of the reaction do not change with time.

Conditions for Attainment of Chemical Equilibrium

In a reversible reaction, reactant molecules react to give products and at the same time some product molecules give back reactants. The rate of reaction depends upon the concentration of reactants. The rate of forward reaction depends upon the concentration of reactants while the rate of reverse reaction depends upon the concentration of products as shown in Figure 5.1. Initially only the reactants are present, therefore, the rate of forward reaction is fast. The reaction in the reverse direction does not take place as no product is present. As the reaction progresses, due to the decrease in the concentration of reactants, the rate of forward reaction decreases. At the same time, due to the increase in the concentration of products, the rate of reverse reaction increases. As the reaction further progresses a stage is reached when the rate of forward reaction becomes equal to the rate of reverse reaction. When this stage is attained, the concentrations of reactants and products do not change. The reaction has attained chemical equilibrium.

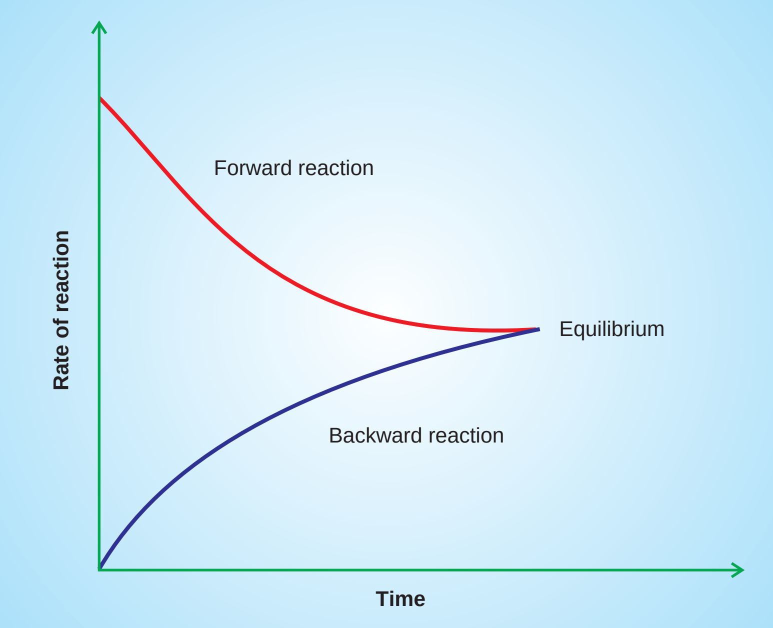


Fig 5.1 Change in the rate of reaction with time for the forward and reverse reactions.

For example, as seen earlier, formation of ammonia from nitrogen and hydrogen is a reversible process. At the start of the reaction only nitrogen and hydrogen are present. They combine to form ammonia. The rate of formation of ammonia is large. With the progress of reaction, the concentrations of nitrogen and hydrogen decrease so the rate of formation of ammonia decreases. As more and more ammonia molecules are formed, some of the molecules start decomposing to give back nitrogen and hydrogen. With the progress of reaction, the number of ammonia molecules increases, so the rate of decomposition of ammonia also increases. As the reaction proceeds, the rate of formation of ammonia decreases while the rate of decomposition of ammonia increases. A stage is reached when the two rates become equal and equilibrium is attained.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The chemical equilibrium is also dynamic in nature since the reaction does not stop at equilibrium. The macroscopic properties remain constant because the rate of forward reaction becomes equal to the rate of reverse reaction and hence no net reaction takes place.

Another example is the decomposition of dinitrogen tetraoxide to form nitrogen dioxide.

$$\underset{\text{colourless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{reddish brown}}{2NO_2(g)}$$

When colourless N_2O_4 is taken in a closed vessel, after some time its colour changes to brown indicating that NO_2 has been formed.

Similarly, if NO_2 is taken in a closed vessel, initially the colour is reddish brown but the colour starts fading and after some time it becomes brown. This colour change takes place because some NO_2 molecules dimerize to form N_2O_4.

In both the cases, the final colour is same indicating that at equilibrium both N_2O_4 and NO_2 are present.

From these observations it can be concluded that the chemical equilibrium is attained whether the reaction is started with reactants or with products. That is, chemical equilibrium can be obtained from forward direction as well as reverse direction.

It should be noted that the concentrations of products and reactants are not necessarily equal at equilibrium, only the rate of forward and reverse reactions are equal.

Characteristics of Chemical Equilibrium

The reaction is reversible in nature.

- The reaction takes place in a closed vessel, that is, during the reaction; reactants and products are neither added nor removed from the reaction vessel.
- The rate of forward reaction is equal to the rate of reverse reaction.
- All the reactants and products are present at equilibrium.
- The macroscopic properties like temperature, pressure, volume and concentration do not change with time.
- The equilibrium is dynamic in nature.
- The state of equilibrium can be obtained from either side.
- The concentrations of reactants and products are generally not equal.
- The free energy change of the reaction is zero at equilibrium.

Exercise 5.2

Answers the following questions:

1. When a mixture of SO_2 and O_2 is introduced into a reaction vessel at a temperature of 700 K, a reaction that produces SO_3 occurs as:

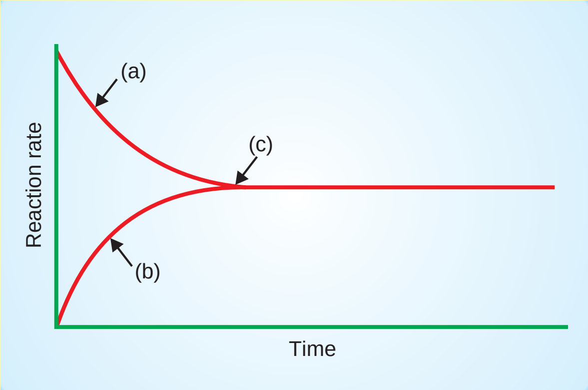
$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

   a When do we say that the system has reached chemical equilibrium? Explain your answer.

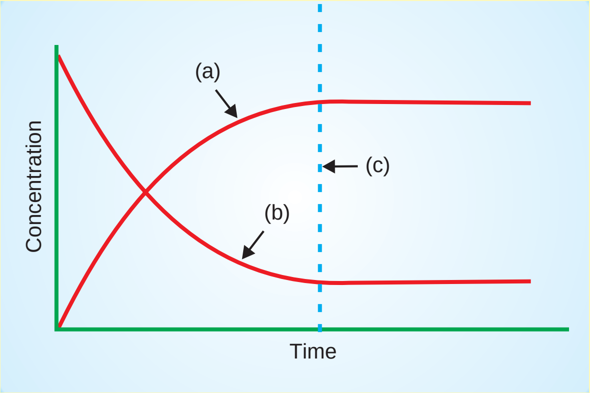
   b Why is the equilibrium state referred to as dynamic?

   c Write the equation that shows the presence of the three species in equilibrium.

2. Label a, b and c for the figure below. Explain trends of the rate of the forward reaction and the rate of the reverse reaction.



3. Label a, b and c for the figure shown below. Explain what happens to the concentration of the reactants and the concentration of the products.



4. What are the conditions that remain constant at equilibrium?

5.1.3 Equilibrium Expression and Equilibrium Constant

Law of Mass Action

Two Norwegian scientists C.M. Guldberg and Peter Waage studied reversible chemical reactions and gave a law characterizing the dynamic chemical equilibrium. This law is known as law of mass action. According to this law:

- The combining power of two reactants A and B depends upon their nature as well as their active concentrations.
- The rate at which A and B combine is directly proportional to the product of their concentration terms each raised to the power of its respective coefficient in the balanced chemical reaction.

The general equation that represents a reversible reaction is:

$$aA + bB \rightleftharpoons mM + nN$$

For the forward reaction A and B are reactants and M and N are products.

It is assumed that the reaction is homogeneous in nature, that is all the reactants and the products are present in the same state.

The rate of forward reaction (r_f) depends upon the concentrations of A and B and is given by the expression

$$r_f \propto [A]^a\,[B]^b \qquad \text{or} \qquad r_f = k_f\,[A]^a\,[B]^b$$

where [A] and [B] are the concentrations of A and B respectively. The rate of reverse reaction is given by the expression

$$r_b \propto [M]^m\ [N]^n \qquad \text{or} \qquad r_b = k_b\ [M]^m\ [N]^n$$

where [M] and [N] are the concentrations of M and N respectively. k_f and k_b are rate constants for forward and reverse reactions, respectively.

At equilibrium, the rate of forward reaction is equal to the rate of reverse reaction. Therefore,

$$r_f = r_b$$

or

$$k_f\ [A]^a\ [B]^b = k_b\ [M]^m\ [N]^n$$

k_f and k_b are constant. Therefore, the ratio of k_f to k_b is also a constant.

$$\frac{k_f}{k_b} = \frac{[M]^m\ [N]^n}{[A]^a [B]^b} = K_{eq}$$

The ratio of k_f and k_b is represented by K_{eq}. Since this constant represents the reaction at equilibrium it is known as equilibrium constant. [M], [N], [A] and [B] are concentrations at equilibrium.

When the concentrations are expressed in molarities, the equilibrium constant is represented by K_c.

When the reactants and the products are in the gaseous state, their concentrations can be expressed in terms of partial pressures. In such cases, the equilibrium constant is denoted by K_p.

Rules for Writing the Equilibrium Constant Expression for Homogeneous Reactions

Homogeneous reaction is a reaction in which all the reactants and the products are present in the same physical state.

For a homogeneous reaction, rules followed while writing the expression for equilibrium constant are:

- The concentrations of all the substances formed as products are written in the numerator.
- The concentrations of all the reactants are written in the denominator.

- Each concentration term is raised to the power by its respective coefficient as written in the balanced chemical reaction.

For a general reaction at equilibrium

$$aA + bB \rightleftharpoons mM + nN$$

the expression for K_c is:

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

When all the reactants and the products are in the gaseous state, their concentrations can be written in terms of partial pressures. In such cases the equilibrium constant is denoted by K_p. The expression for K_p is

$$K_p = \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b}$$

For the formation of ammonia,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the expression of equilibrium constant in terms of molarities is:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

The expression of K_p is:

$$K_p = \frac{\left(p_{NH_3}\right)^2}{\left(p_{N_2}\right)\left(p_{H_2}\right)^3}$$

Exercise 5.3

Write the equilibrium constant expression for the following reactions:

1. $NH_3(g) + CH_3COOH(aq) \rightleftharpoons NH_4^+(aq) + CH_3COO^-(aq)$
2. $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
3. $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$
4. $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$

Units of K_c

The unit of K_c of a reaction depends upon the number of moles of the reactants and products involved in the reaction. Therefore, for a general reaction;

$$aA + bB \rightleftharpoons mM + nN$$

the unit of K_c will be:

$$K_c = \frac{[M]^m[N]^n}{[A]^a[B]^b} = \frac{[\text{mol L}^{-1}]^m\,[\text{mol L}^{-1}]^n}{[\text{mol L}^{-1}]^a[\text{mol L}^{-1}]^b} = (\text{mol L}^{-1})^{(m+n)-(a+b)}$$

Example 5.1

1. For the reaction:

$$NH_3(g) + CH_3COOH(aq) \rightleftharpoons NH_4^+(aq) + CH_3COO^-(aq)$$

$$K_c = \frac{\left[NH_4^+\right]\left[CH_3COO^-\right]}{[NH_3][CH_3COOH]} = \frac{\left(\text{mol L}^{-1}\right)\left(\text{mol L}^{-1}\right)}{\left(\text{mol L}^{-1}\right)\left(\text{mol L}^{-1}\right)} = 1$$

2. For the reaction:

$$2HF(g) \rightleftharpoons H_2(g) + F_2(g)$$

$$K_c = \frac{\left[H^+\right]\left[F^-\right]}{[HF]} = \frac{\left(\text{mol L}^{-1}\right)\left(\text{mol L}^{-1}\right)}{\left(\text{mol L}^{-1}\right)} = \text{mol L}^{-1}$$

Unit of K_p

The unit of K_p is decided by the unit of pressure. If the partial pressure is expressed in atm, then the unit of K_p, will be:

$$K_p = \frac{(p_M)^m\,(p_N)^n}{(p_A)^a\,(p_B)^b} = \frac{(\text{atm})^m\,(\text{atm})^n}{(\text{atm})^a\,(\text{atm})^b} = (\text{atm})^{(m+n)-(a+b)}$$

If the partial pressure is measured in kPa, then the unit of K_p will be $(\text{kPa})^{(m+n)-(a+b)}$

Example 5.2

K_p units for the following reactions are shown.

1. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_p = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \dfrac{\text{atm}^2}{\text{atm}\cdot\text{atm}^3} = \dfrac{1}{\text{atm}^2}$

2. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_p = \dfrac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \dfrac{(\text{atm})^2}{(\text{atm})(\text{atm})} = 1$

3. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_p = \dfrac{(P_{NO_2})^2}{(P_{N_2O_4})} = \dfrac{(\text{atm})^2}{(\text{atm})} = \text{atm}$

Equilibrium Constant for Heterogeneous Reactions

Activity 5.4

Form a group and discuss the following questions:

Consider the reaction

$$Mg(s) + HCl(aq) \rightleftharpoons MgCl_2(aq) + H_2(g)$$

1. Identify the phases of the reactants and the products. Are the reactants and the product in the same or different phases?
2. What is the name of the equilibrium that involves such reactants and the product?

Share your ideas with the rest of the class.

In heterogeneous reactions, the reactants and products are present in more than one physical state. For example, thermal decomposition of calcium carbonate is an example of heterogeneous reaction.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Some other examples of heterogeneous reactions are

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

$$CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Rules for Writing the Expression for Equilibrium Constant for Heterogeneous Reaction

- The concentration terms of products are written in the numerator and the concentration terms of reactants are written in the denominator raised to the power of their respective coefficient in the balanced chemical equation.
- While writing the expression for K_c, the molarities of gaseous reactants and products and species present in the solution are written.
- Concentration terms of solids and pure liquids do not appear in the expression, as they are taken to be unity.
- While writing the expression for K_p, partial pressures of only the gaseous reactants and products are written in the expression for equilibrium constant.

Example 5.3

The equilibrium constant expression for some heterogeneous reactions are shown below:

a $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K_p = p_{CO_2}$

b $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ $K_p = (p_{NH_3})(p_{HCl})$

c $CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ $K_c = \dfrac{\left[H^+\right]\left[HCO_3^-\right]}{\left[CO_2\right]}$

d $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$ $K_c = \dfrac{1}{\left[Fe^{3+}\right]\left[OH^-\right]^3}$

Exercise 5.4

Answer the following questions:

1. 5.0 mole of ammonia were introduced into a 5.0 L reaction chamber in which it is partially decomposed at high temperatures.

$$2NH_3(g) \rightleftharpoons 3H_2(g) + N_2(g)$$

At equilibrium at a particular temperature, 80.0% of the ammonia had reacted. Calculate K_c for the reaction.

2. 1.25 mol NOCl was placed in a 2.50 L reaction chamber at 427°C. After equilibrium was reached, 1.10 moles NOCl remained. Calculate the equilibrium constant for the reaction.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

3. A sample of nitrosyl bromide was heated to 100°C in a 10.0 L container in order to partially decompose it.

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

At equilibrium the container was found to contain 0.0585 mol of NOBr, 0.105 mol of NO, and 0.0524 mol of Br_2. Calculate the value of K_c.

4. The brown gas NO_2 and the colourless gas N_2O_4 exist in equilibrium.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

0.625 mol of N_2O_4 was introduced into a 5.00 L vessel and was allowed to decompose until it reached equilibrium with NO_2. The concentration of N_2O_4 at equilibrium was 0.0750 M. Calculate K_p for the reaction.

Relation between K_c and K_p

For the general reaction

$$a\,A(g) + bB(g) \rightleftharpoons mM(g) + nN(g)$$

$$K_c = \frac{[M]^m[N]^n}{[A]^a[B]^b} = \frac{C_M^m C_N^n}{C_A^a C_B^b}$$

$$K_p = \frac{(p_M)^m(p_N)^n}{(p_A)^a(p_B)^b}$$

It is assumed that all the gaseous species behave like an ideal gas. According to the ideal gas equation, the partial pressure (p) is given by

$$p = nRT\,/\,V \qquad \text{and} \qquad n/V = C$$

where n = amount of the gaseous species in moles

R = Gas constant

T = Temperature in kelvin

V = Volume of the reaction mixture

C = Molarity

Thus, $p_A = n_A RT / V \quad = C_A RT$

$p_B = n_B RT / V \quad = C_B RT$

$p_M = n_M RT / V \quad = C_M RT$

$p_N = n_N RT / V \quad = C_N RT$

$$K_p = \frac{(C_M RT)^m (C_N RT)^n}{(C_A RT)^a (C_B RT)^b} = \frac{C_M^m C_N^n}{C_A^a C_B^b}(RT)^{\Delta n}$$

here $\Delta n = (m + n) - (a + b)$ for gaseous species

$$K_p = K_c (RT)^{\Delta n}$$

When the number of gaseous reactants and products are equal then,

$$a + b = m + n$$

Therefore, $\Delta n = 0$ and hence $K_p = K_c$

Example 5.4

1. The equilibrium constant for the reaction:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

is 1.8×10^{-3} kPa at 427°C. Calculate K_c for the reaction at the same temperature.

Solution:

Given: $K_p = 1.8 \times 10^{-3}$ kPa $= 1.8$ Nm^{-2} $\quad T = 427°C = 700$ K.

$R = 8.314$ N m K^{-1} mol^{-1}

We know that

$$K_p = K_c (RT)^{\Delta n}$$

For the given reaction, $\Delta n = (2+1) - 2 = 1$

Therefore, $K_c = K_p / (RT)$

$$= \frac{1.8\ \text{Nm}^{-2}}{700\ \text{K} \times 8.314\ \text{N m K}^{-1}\text{mol}^{-1}} = 3.09\ \text{mol m}^{-3}$$

2. What are the values of K_p and K_c at 1000°C for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

if the pressure of CO_2 in equilibrium with $CaCO_3$ and CaO is 3.87 atm?

Enough information is given to find K_p first. Writing the K_p expression for this heterogeneous reaction:

$$K_p = p_{CO_2} = 3.87$$

Then to get K_c, rearrange the equation,

$$K_p = K_c(RT)^{\Delta n}$$

where n, the change in the number of moles of gas in the reaction is +1.

Calculation:

$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$K_c = \frac{3.87}{(0.0821)(1273)} = 0.0370$$

3. At 400 °C, K_c = 64 for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

a What is the value of K_p for this reaction?

b If at equilibrium, the partial pressures of H_2 and I_2 in a container are 0.20 atm and 0.50 atm, respectively, what is the partial pressure of HI in the mixture?

Solution:

a The equation relating K_p to K_c is

$$K_p = K_c(RT)^{\Delta n}$$

Here the change in the number of moles of gas Δn is:

$$\Delta n = 2 \text{ mol HI} - 1 \text{ mol } H_2 - 1 \text{ mol } I_2 = 0$$

Since, $\Delta n = 0$, K_p and K_c are the same.

$$K_p = K_c(RT)^0 = K_c$$

$$K_p = K_c = 64$$

b Writing the equilibrium constant expression

$$K_p = \frac{p^2_{HI}}{p_{H_2}\, p_{I_2}} = 64$$

and substituting the given pressures

$$\frac{p^2_{HI}}{(0.20)(0.50)} = 64$$

the partial pressure of HI is

$$p_{HI} = \sqrt{(0.20)(0.50)(64)}$$

$$p_{HI} = 2.53 \text{ atm}$$

Exercise 5.5

Answers the following questions:

1. The following equilibrium constants were determined at 1123 K:

   $C(s) + CO_2(g) \rightleftharpoons 2CO(g) \qquad K_c = 1.4 \times 10^{12}$

   $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad K_c = 5.5 \times 10^{-1}$

   Write the equilibrium constant expression K_c and calculate the equilibrium constant at 1123 K for the following reaction:

   $C(s) + CO_2(g) + 2Cl_2(g) \rightleftharpoons 2COCl_2(g)$

2. For the decomposition of ammonium chloride,

   $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ at 427°C, $K_p = 4.8$.

   Calculate K_c for this reaction.

3. Write the equilibrium constant expression for the following equations:

   a $2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$

   b $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$

   c $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$

4. For the reaction:

   $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

   $K_p = 7.1 \times 10^4$ at 700 K. What is the value of K_p for the following reactions at the same temperature?

   a $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

   b $\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(g) \rightleftharpoons HBr(g)$

5. The reversible reaction:

   $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

   has a value of $K_p = 0.113$ at 25°C. Determine the numerical value of K_c at 25°C for the reaction,

   $\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g)$

   Is it greater than, equal to, or less than 0.113? Explain.

Applications of Equilibrium Constant

Activity 5.5

Form a group and discuss the following:

The equilibrium constant, K_c for the formation of hydrogen iodide from molecular hydrogen and molecular iodine in the gas phase

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

is 54.3 at 430°C. Suppose that in a certain experiment we place 0.243 mole of H_2, 0.146 mole of I_2, and 1.98 moles of HI all in a 1.00 L container at 430°C. Will there be a net reaction to form more H_2 and I_2 or more HI?

Share your ideas with the rest of the class.

The value of equilibrium constant predicts the extent of reaction at equilibrium. It also tells about the relative concentrations of products and reactants present at equilibrium, that is, the position of equilibrium.

Position of equilibrium: K_c can have three types of values.

Case 1: When $K_c > 1$

This indicates that the value of numerator is greater than the denominator. So the formation of products is favoured at equilibrium.

Case 2: When $K_c < 1$

This indicates that the value of numerator is less than the denominator. So the formation of products is not favoured at equilibrium.

Case 3: When $K_c = 1$

This indicates that the rate of forward reaction is equal to the rate of backward reaction.

Extent of reaction: K_c value also predicts the extent of the reaction at equilibrium. Very large values of K_c indicates that the extent of the reaction is very large at equilibrium. So most of the reactants have been consumed at equilibrium. A very small value of K_c indicates that the extent of reaction is very small at equilibrium. Most of the reactants will be in the unreacted state.

Activity 5.6

Form a group and discuss the following questions:

1. Predict whether the formation of product is favoured for the following reactions:
   - a $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 3.6 \times 10^8$
   - b $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_c = 5 \times 10^{-3}$
   - c $CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ $K_c = 4.45 \times 10^{-24}$
2. Arrange the following reactions in order of their increasing tendency to proceed towards completion (least extent to greatest extent).
   - a $CO + Cl_2 \rightleftharpoons COCl_2$ $K_c = 13.8$
   - b $N_2O_4 \rightleftharpoons 2NO_2$ $K_c = 2.1 \times 10^{-4}$
   - c $2NOCl \rightleftharpoons 2NO + Cl_2$ $K_c = 4.7 \times 10^{-4}$

Share your ideas with the rest of the class.

Reaction Quotient (Q)

Reaction quotient is the ratio of concentrations of products to the concentrations of reactants raised to the power of their respective coefficients at any stage after the start of the reaction. For the general reaction,

$$aA + bB \rightleftharpoons mM + nN$$

the expression for the reaction quotient is

$$Q = \frac{[M]^m[N]^n}{[A]^a[B]^b}$$

[A], [B], [M] and [N] are concentrations at any stage during the reaction. At the initial stages of the reaction, the amount of product formed is low, therefore, the value of Q is small. With the progress of the reaction, since the concentration of products increases, the value of Q also increases. When the reaction attains equilibrium, Q becomes equal to the equilibrium constant.

Reaction Quotient in Terms of Molarities

When the concentrations are expressed in molarities, the reaction quotient is Q_c.

$$Q_c = \frac{[M]^m[N]^n}{[A]^a[B]^b}$$

At equilibrium,

$$Q_c = \left\{\frac{[M]^m[N]^n}{[A]^a[B]^b}\right\}_{eq} = K_c$$

Reaction Quotient in Terms of Partial Pressure

When the concentrations are taken in partial pressures, the reaction quotient is Q_p and is given by the expression

$$Q_p = \frac{(p_M)^m(p_N)^n}{(p_A)^a(p_B)^b}$$

At equilibrium,

$$Q_p = \left\{\frac{(p_M)^m(p_N)^n}{(p_A)^a(p_B)^b}\right\}_{eq} = K_p$$

Application of Reaction Quotient

Reaction quotient predicts the direction of the reaction at any stage, that is for the given concentration of reactants and products. It also decides whether the reaction has attained equilibrium or not.

When Q is less than K, then the reaction will proceed in the forward direction and more products will be formed till the equilibrium is reached.

When Q is greater than K, then the reaction will proceed in the reverse direction and more reactants will be formed till the equilibrium is reached.

When Q is equal to K, then the reaction has attained equilibrium.

Example 5.5

At a certain temperature the reaction:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

has an equilibrium constant K_c = 13.8. Is the following mixture an equilibrium mixture? If not, in which direction (forward or backward) will the reaction proceed to reach equilibrium? $[CO]_0$ = 2.5 mol L^{-1}; $[Cl_2]_0$ = 1.2 mol L^{-1}; and $[COCl_2]_0$ = 5.0 mol L^{-1}.

Solution:

Recall that for the system to be at equilibrium $Q_c = K_c$. Substitute the given concentrations into the reaction quotient for the reaction, and determine Q_c.

$$Q_c = \frac{5\ \text{mol L}^{-1}}{(2.5\ \text{mol L}^{-1})(1.2\ \text{mol L}^{-1})} = 1.6\left(\text{mol L}^{-1}\right)^{-1}$$

Since $Q_c < K_c$ the reaction mixture is not an equilibrium mixture, and a net forward reaction will bring the system to equilibrium.

Calculating the Equilibrium Concentrations

Not only can we estimate the extent of reaction from the K_c value, but also the expected concentrations at equilibrium can be calculated from knowledge of the initial concentrations and the K_c value. In these types of problem it will be very helpful to use the following approach.

1. Express the equilibrium concentrations of all the species in terms of the initial concentrations and an unknown x, which represents the change in concentration.

2. Substitute the equilibrium concentrations derived in part 1 into the equilibrium constant expression, and solve for x. The equilibrium concentration is given by: equilibrium concentration = initial concentration ± the change due to the reaction where the + sign is used for a product, and the – sign for a reactant.

3. Use x to calculate the equilibrium concentration of all the species.

Example 5.6

Let us consider the reactioin between hydrogen and iodine in which 1 mole of H_2 and 2 moles of I_2 were added in 500 mL flask. First we need expressions for the equilibrium concentrations of H_2, I_2, and HI. Tabulating the initial concentrations as:

Concentration	H_2	+	I_2	$\rightleftharpoons$	**2HI**
Initial	1.00 mol/0.50 L		2.00 mol/0.50 L		0
Change	–		–		–
Equilibrium	–		–		–

Since the answer involves three unknowns, we will relate the concentrations to each other by introducing the variable x. Recall, that the equilibrium concentration = initial concentration ± change in concentration. Let x = the change in concentration of H_2. That is, let x = the number of moles of H_2 reacting per liter. From the coefficients of the balanced equation we can tell that if the change in H_2 is $-x$, then the change in I_2 must also be $-x$, and the change in HI must be $+2x$.

The next step is to complete the table in units of molarity:

Concentration	H_2	+	I_2	$\rightleftharpoons$	**2HI**
Initial (M)	2.0		4.0		0
Change (M)	$-x$		$-x$		
Equilibrium (M)	$(2.0 - x)$		$(4.0 - x)$		$+2x$

Now substitute the equilibrium concentrations from the table into the K_c expression,

$$K_c = \frac{(2x)^2}{(2.0 - x)(4.0 - x)}$$

and solve for x.

$$K_c = \frac{(2x)^2}{x^2 - 6.0x + 8.0} = 64$$

Rearranging, we get:

$$4x^2 = 64x^2 - 384x + 512$$

and grouping yields

$$60x^2 - 384x + 512 = 0$$

We will use the general method of solving a quadratic equation of the form

$ax^2 + bx + c = 0$

The root x is given by

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, $a = 60$, $b = -384$, and $c = 512$. Therefore,

$$x = \frac{-(-384) \pm \sqrt{(-384)^2 - 4(60)(512)}}{2(60)}$$

$$x = \frac{384 \pm \sqrt{2.5 \times 10^4}}{120}$$

$$x = \frac{384 \pm 158}{120} = 1.9 \text{ and } 4.5 \text{ mol/L}$$

Recall that x = the number of moles of H_2 (or I_2) reacting per liter. Of the two answers (roots), only 1.9 is reasonable, because the value 4.5 M would mean that more H_2 (or I_2) reacted than was present at the start. This would result in a negative equilibrium concentration, which is physically meaningless. We therefore use the root x = 1.9 M to calculate the equilibrium concentrations:

$[H_2] = 2.0 - x = 2.0\text{ M} - 1.9\text{ M} = 0.1\text{ M}$

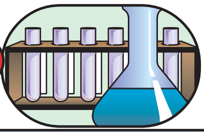
$[I_2] = 4.0 - x = 4.0\text{ M} - 1.9\text{ M} = 2.1\text{ M}$

$[HI] = 2x = 2(1.9\text{ M}) = 3.8\text{ M}$. The results can be checked by inserting these concentrations back into the K_c expression to see if $K_c = 64$.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(3.8)^2}{(0.1)(2.1)} = 68$$

Thus the concentrations we have calculated are correct. The difference between 64 and 68 results from rounding off which is to maintain the correct number of significant figures. Therefore, our result is correct only to the number of significant figures given in the problem.

Experiment 5.1



Determination of Equilibrium Constant for an Organic Acid

Objective: To determine equilibrium constant for the esterification of an acetic acid.

Apparatus: Round bottom flask, pipette, conical flask, burette, burette stand, water condenser with inlet and outlet pipes, boiling chips, clamp stand, burner, water bath.

Chemicals: 0.5 M acetic acid, 0.5 M propan-1-ol, phenolphthalein, 0.01 M NaOH solution, ice.

Procedure:

1. In a 100 mL round bottom flask, take 10.0 mL of 0.5 M acetic acid and 10.0 mL of 0.5 M propan-1-ol.
2. Add 5 drops of conc. H_2SO_4 to the solution in the round bottom flask.
3. Add a few pieces of boiling chips to the solution in the round bottom flask.
4. Attach a water condenser and reflux for 1 hour on a water bath as shown in (Figure 5.2(a)).
5. Cool the flask and its contents in an ice bath.
6. Pipette out 1.0 mL of the reaction mixture in a conical flask containing 25.0 mL of ice cold water. (Ice cold water is prepared by taking 25.0 mL of water in a conical flask and keeping on ice bath for some time).
7. Add 2 drops of phenolphthalein indicator to the solution in a conical flask.
8. Titrate the contents against 0.1 M NaOH solution as shown in (Figure 5.2(b)).
9. Repeat steps 6, 7 and 8 three times and take the average volume of NaOH consumed in titration.

Observations and analysis:

1. What is the purpose of adding small amount of H_2SO_4 to the reaction mixture at one beginning of the experiment?
2. Why do we add boiling chips to the reaction mixture before refluxing?
3. Calculate:
   a the concentrations of reactions and products at equilibrium.
   b the equilibrium constant for the esterification of acetic acid.

Hint: The esterification reaction is acid catalysed.

$$CH_3COOH(aq) + CH_3CH_2CH_2OH(aq) \rightleftharpoons CH_3COOC_3H_7(aq) + H_2O(aq)$$

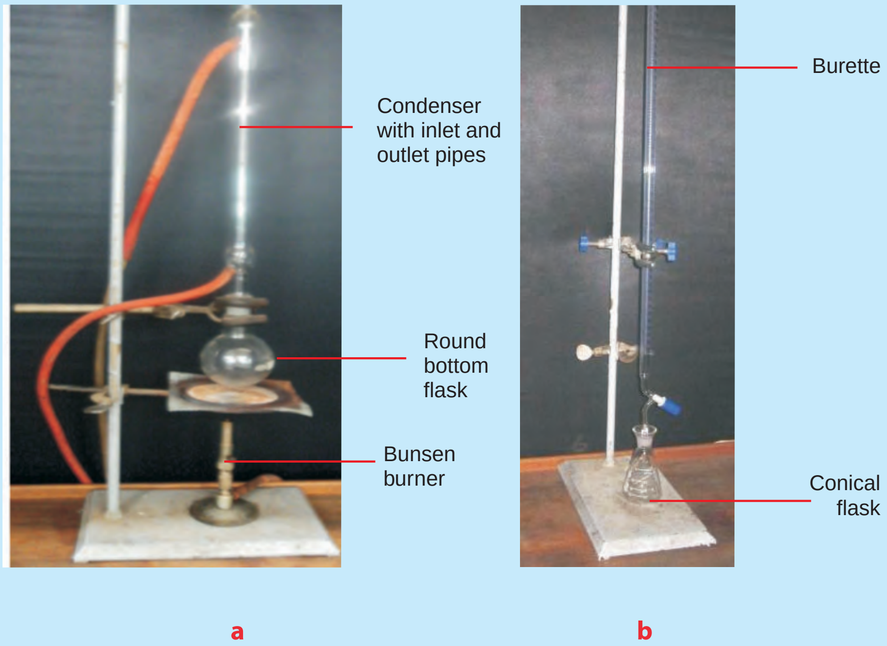


Figure 5.2 Laboratory set-up for the esterification of acetic acid.

Exercise 5.6

1. For the equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 0.36 \text{ at } 100°C$$

a sample of 0.25 mol N_2O_4 is allowed to dissociate and come to equilibrium in a 1.5 L flask at 100°C. What are the equilibrium concentrations of NO_2 and N_2O_4?

2. The decomposition of NOBr is represented by the equation:

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g) \qquad K_c = 0.0169$$

At equilibrium the concentrations of NO and Br_2 are 1.05×10^{-2} M and 5.24×10^{-3} M, respectively. What is the concentration of NOBr?

3. The reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

has the equilibrium constant value $K_c = 0.24$ at 300 °C.

   a Is the following reaction mixture at equilibrium?

   $[PCl_5] = 5.0$ mol/L, $[PCl_3] = 2.5$ mol/L, $[Cl_2] = 1.9$ mol/L

   b Predict the direction in which the system will react to reach equilibrium

4. At 400°C, the equilibrium constant for the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 64. A mixture of 0.250 mol H_2 and 0.250 mol I_2 was introduced into an empty 0.75 L reaction vessel at 400°C, find the equilibrium concentrations of all components

5. At 700 K, the reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

has an equilibrium constant $K_c = 4.3 \times 10^6$.

   a Is a mixture with the following concentrations at equilibrium?

   $[SO_2] = 0.10$ M; $[SO_3] = 10$ M; $[O_2] = 0.10$ M.

   b If not at equilibrium, predict the direction in which a net reaction will occur to reach a new equilibrium.

5.1.4 Changing Equilibrium Conditions–Le Chatelier's Principle

Activity 5.7

Form a group and discuss the following questions:

1. Consider the following reaction at 400°C:

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Some amounts of H_2O, CO(g), $H_2(g)$, and $CO_2(g)$ were put into a flask so that the composition corresponded to an equilibrium mixture. A laboratory technician added an iron catalyst to the mixture, but was surprised when no additional H_2(g) and CO_2(g) were formed even after waiting for many days. Explain why the technician should not have been surprised.

2. Equilibrium is established in the reversible reaction

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g) \qquad \Delta H = 114.4 \text{ kJ}$$

Describe four changes that could be made to this mixture to increase the amount of Cl_2(g) at equilibrium.

3. Describe how you might be able to drive a reaction having a small value of K_c to completion.

Share your ideas with the rest of the class.

Factors Affecting the Equilibrium Constant

The equilibrium constant depends upon the following factors:

1. Temperature at which the experiment is performed.
2. The form of equations which describe the equilibrium.

For example, for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

If the reaction is multiplied by 2,

$$2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$$

the expression for K_c becomes

$$K_c' = \frac{[NH_3]^4}{[N_2]^2[H_2]^6}$$

$$K_c' = (K_c)^2$$

If the reaction is reversed, $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

the K_c becomes

$$K_c'' = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$K_c'' = 1/K_c$$

The equilibrium constant does not depend upon the initial concentrations of the reactants. K_c and K_p are independent of pressure.

Le Chatelier's Principle

When the reaction has attained equilibrium then the temperature, pressure, volume and concentrations remain constant. These four properties are known as reaction parameters. Le Chatelier's principle describe the changes that will take place when any one of the reaction parameters are changed at equilibrium.

Statement: If any one or more of the reaction parameters is changed at equilibrium then the reaction will proceed in that direction so as to undo the change in the parameter and the equilibrium is again attained.

Le Chatelier's principle describes the effect of the change in parameters on the position of equilibrium. That is, it predicts whether the changes in reaction parameters will favour the formation of reactants or products.

Historical Note

Henry Louis Le Chatelier

Henry Louis Le Chatelier (1850-1936) was a French-Italian chemist. He is most famous for the law of chemical equilibrium which is known by his name as Le Chatelier's principle. This law is used by chemists to predict the effect of a change in conditions on a chemical equilibrium

Effect of Change in Temperature on the Position of Equilibrium

Activity 5.8

Form a group and perform the following activity to study the effect of temperature on the position of equilibrium:

Take 0.5 g of cobalt chloride ($CoCl_2{\cdot}6H_2O$) in a test tube and add 10 mL of distilled water to prepare the solution. Then add 5 mL of concentrated HCl slowly to the solution. What is the colour of the solution? Now put the test tube in a beaker containing crushed ice. Note the colour of the solution. Take out the test tube from ice bath and keep it at room temperature for 5 minutes. Note the colour of the solution.

Share your findings with the rest of the class.

According to Le Chatelier's principle, if the temperature of the reaction at equilibrium is increased then the reaction will proceed in that direction where heat is absorbed so as to undo the effect of heating. Similarly if the temperature of the reaction at equilibrium is lowered then the reaction will proceed in that direction where the heat is produced so that the equilibrium is again attained.

For an exothermic reaction, when the temperature is lowered, the reaction will proceed in the forward direction, since the heat produced during forward reaction will undo the effect of lowering of temperature. When the temperature is increased, then the reaction will proceed in the reverse direction where the heat is absorbed.

For an endothermic reaction, when the temperature is lowered, the reaction will proceed in the reverse direction where heat is produced so as to undo the effect of lowering of temperature. When the temperature is increased, the reaction proceeds in the forward direction.

Effect of temperature in terms of amount of reactants and products formed can be summarized as:

When the equilibrium shifts in the forward direction, then the concentration of products increases and that of reactants decreases.

So for exothermic reactions when the temperature is lowered, more products are formed. That is, the decrease in temperature favours exothermic reactions.

For endothermic reactions, when the temperature is increased, more products are formed, That is, increase in temperature favours endothermic reactions.

For example, formation of ammonia is an exothermic process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

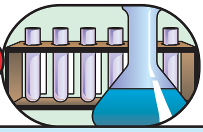
If the temperature is lowered at equilibrium, the reaction will proceed in the forward direction till the new equilibrium is established. So the concentration of ammonia will increase. If the temperature is increased at equilibrium, then the reaction will proceed in reverse direction which is endothermic in nature. So the concentration of ammonia will decrease.

Dissociation of dinitrogen tetroxide is endothermic in nature.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Therefore, according to Le Chatelier's principle, the formation of NO_2 is favoured by increase in the temperature at equilibrium.

Experiment 5.2



Effect of Change in Temperature on the Equilibrium Position

Objective: Determination of the effect of changes in temperature on the position of equilibrium of iodine and starch.

Apparatus: Test tubes, water bath, stands, Bunsen burner, thermometer.

Chemicals: Iodine, starch.

Procedure:

1. Add a few drops of tincture of iodine to some starch solution in a test tube. Record your observations.
2. Heat the solution to about 80°C using a water bath. Record your observation. What can we deduce from this?
3. Cool the container by placing it in an ice box. Record your observation.

Observations and analysis:

1. Explain the concept of a starch-iodine complex. Is this an example of an equilibrium reaction?
2. Which direction is exothermic and which is endothermic? How do you explain your results?
3. What can you conclude based on your observations?

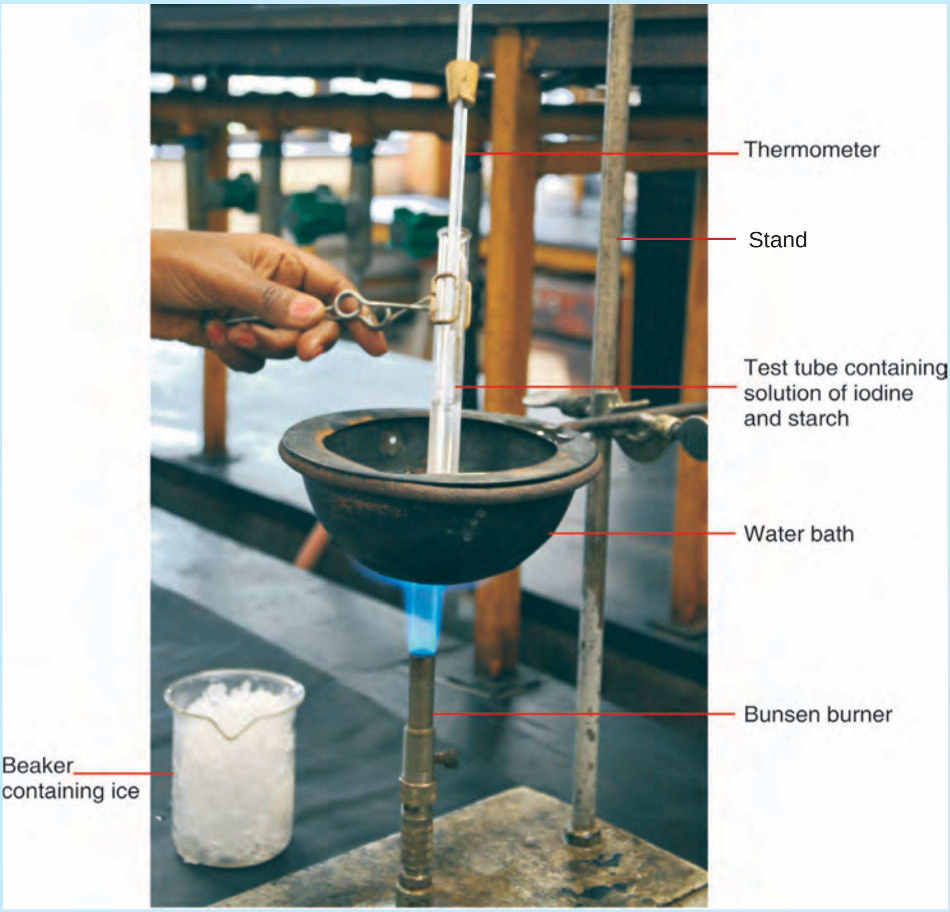


Figure 5.3 Laboratory set-up for the effect of changes in temperature on equilibrium of iodine and starch.

Effect of Change in Pressure on the Position of Equilibrium

According to Le Chatelier's principle, if the pressure at equilibrium is increased then the reaction will proceed in that direction where the pressure is reduced. Since the pressure depends upon the number of moles, on increasing the pressure the reaction will proceed in that direction where the number of moles are reduced.

If the pressure at equilibrium is decreased then the reaction will proceed in that direction where the number of moles is more.

For a general reaction,

$$aA + bB \rightleftharpoons mM + nN$$

the effect of pressure is decided by Δn.

$$\Delta n = (m + n) - (a + b)$$

If $\Delta n > 0$, that means the total moles of products is greater than the total moles of reactants. Lowering of pressure will favour the reaction in forward direction. That is, more products will be formed at equilibrium if the pressure is lowered.

If $\Delta n < 0$, that means the total moles of products is less than the total moles of reactants. Increasing the pressure will favour the reaction in forward direction. That is, more products will be formed at equilibrium if the pressure is increased.

If $\Delta n = 0$, then the change in pressure has no effect on the position of equilibrium.

For example, in the formation of ammonia,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$\Delta n = 2-(1+3) = -2$$

Therefore, an increase in pressure at equilibrium will favour the forward reaction.

For the dissociation of dinitrogen tetroxide, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$\Delta n = 2 - 1 = 1$$

The decrease in pressure at equilibrium, favours the forward reaction.

Hydrolysis of ester is not affected by the change in pressure. Why is it so?

Effect of Change in the Concentration on the Position of Equilibrium

Activity 5.9

Form a group and consider the following reaction at 400°C:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

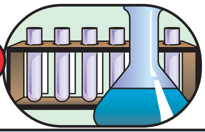
H_2 and I_2 were placed into a flask and allowed to react until equilibrium was reached. Then a small amount of $H^{131}I$ was added. ^{131}I is an isotope of iodine that is radioactive. Discuss whether radioactive ^{131}I will remain in the HI molecule or some, or all, of it will find its way into the I_2 molecule forming $^{127}I^{131}I$.

Share your ideas with the rest of the class.

At equilibrium, on increasing the amount of a substance, the reaction proceeds in that direction where the substance is consumed. When the amount of the reactants is increased the reaction proceeds in the forward direction and when the amount of products is increased, the reaction proceeds in the backward direction.

The forward reaction is favoured if the products formed are removed from the vessel.

Experiment 5.3



Effect of Change in Concentration on Equilibrium Position

Objective: To study the effect of concentration on the position of equilibrium.

Apparatus: Test tubes (5), test tube stand, 100 mL beakers (2),

Chemicals: 0.05 M $Fe(NO_3)_3$ solution, 0.01M KSCN solution, 0.1M HNO_3 acid.

Procedure:

1. Take 5 test tubes and label them as 1, 2, 3, 4 and 5. Keep them on a test tube rack.
2. Take 50 mL of 0.05 M solution of $Fe(NO_3)_3$ in a beaker.
3. In separate beakers take 10 mL of 0.01 M KSCN solution and 20 mL of 0.1 M HNO_3 acid solution.
4. Mix the solutions according to the given table to prepare 5 different solutions.

Test tube No.	**Volume in mL of**		
	0.05 M $Fe(NO_3)_3$	**0.1 M HNO_3**	**0.01 M KSCN**
1	1.0	4.0	1.0
2	2.0	3.0	1.0
3	3.0	2.0	1.0
4	4.0	1.0	1.0
5	5.0	0.0	1.0

5. Note the colour of the solution in each test tube.
6. Arrange the test tubes in the increasing order of colour intensity.

Observations and analysis:

1. Which direction is exothermic and which is endothermic? How do you explain your results?
2. Correlate the colour intensity with the concentration of Fe^{3+} in the test tube.

   Hint: Fe^{3+} forms deep red colour complex with SCN^- ions.

   $$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons \underset{\text{deep red}}{Fe(SCN)^{2+}(aq)}$$

3. By taking different volumes of $Fe(NO_3)_3$ in the test tubes the concentration of Fe^{3+} is varied in the solution. Calculate the concentration of Fe^{3+} ions in each test tube and correlate with the colour intensity.
4. In the test tube take 1.0 mL of $Fe(NO_3)_3$ solution and add 4.0 mL of HNO_3 solution followed by 1.0 mL of KSCN solution. Mix well and note the colour. Add 1.0 mL of $Fe(NO_3)_3$ solution and again note the colour of the solution.

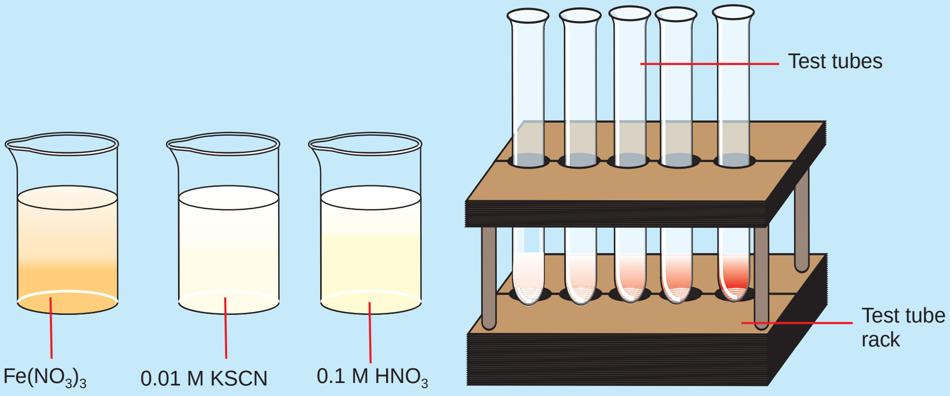


Figure 5.4 Laboratory set-up for the effect of changes in concentration on equilibrium of $Fe^{3+}(aq)$ and $SCN^-(aq)$.

Effect of Catalyst on the Position of Equilibrium

Catalyst is a substance that alters the rate of a reaction without being consumed during the reaction. The catalyst does not effect the position of equilibrium. It alters the time in which the equilibrium is attained. This is due to the fact that the catalyst changes the rate of the forward reaction and the reverse reaction by the same extent so the equilibrium is not effected.

Effect of Addition of Inert Gases on the Position of Equilibrium

When a non reactive gas is added to a reaction at equilibrium, the effect depends on various factors.

Case 1. When the non-reactive gas is added at constant volume there is no change on the position of equilibrium.

Case 2. When the non-reactive gas is added and the volume of the system changes then the effect of position is decided by the stoichiometry of the reaction.

For a general reaction,

$$\text{aA} + \text{bB} \rightleftharpoons \text{mM} + \text{nN}$$

$$\Delta n = (\text{m} + \text{n}) - (\text{a} + \text{b})$$

If $\Delta n < 0$, then the addition of inert gas favours the formation of the reactants.

If $\Delta n > 0$, then the addition of inert gas favours the formation of products.

If $\Delta n = 0$, then the addition of inert gas has no effect on the position of equilibrium.

Example 5.7

For the reaction at equilibrium:

$$2\text{NaHCO}_3(s) \rightleftharpoons \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g) \quad \Delta H^\circ_{rxn} = 128 \text{ kJ}$$

state the effects (increase, decrease, no change) of the following stresses on the number of moles of sodium carbonate, Na_2CO_3, at equilibrium in a closed container. Note that Na_2CO_3 is a solid (this is a heterogeneous equation); its concentration will remain constant, but its amount can change.

a Removing $CO_2(g)$

b Adding $H_2O(g)$

c Raising the temperature

d Adding $NaHCO_3(s)$.

Solution:

a If the CO_2 concentration is lowered, the system will react in such a way as to offset the change. That is, a shift to the right will replace some of the missing CO_2. The number of moles of Na_2CO_3 increases.

b Addition of $H_2O(g)$ exerts a stress on the equilibrium that is partially offset by a shift in the equilibrium to the left (net reverse reaction). This consumes Na_2CO_3 as well as some of the extra H_2O. The number of moles of Na_2CO_3 decreases.

c An increase in temperature will increase the K_c value of an endothermic reaction. There is a shift to the right, and more Na_2CO_3 is formed.

d The position of a heterogeneous equilibrium does not depend on the amount of pure solids or liquids present. The same equilibrium is reached whether the system contains 1 g of $NaHCO_3(s)$ or 10 g of $NaHCO_3$. No shift in the equilibrium occurs. No change in the amount of Na_2CO_3 occurs.

Optimum Conditions

The conditions that give maximum yield of the products are known as optimum conditions. These conditions are decided by the enthalpy of reaction and its stoichiometry applying Le Chatelier's principle.

1. For exothermic reactions the yield of products is increased by performing the reaction at lower temperatures.
2. For endothermic reactions the yield of products is increased by performing the reaction at higher temperatures.
3. When $\Delta n > 0$, the decrease in pressure favours the formation of products.
4. When $\Delta n < 0$, the increase in pressure favours the formation of products.

5. Removing the products from the reaction vessel shifts the equilibrium reaction in the forward direction.

5.1.5 Chemical Equilibrium and Industry

Industrial processes are designed to give maximum possible yield of the products. The conditions for carrying out the reactions are based on Le Chatelier's principle. The following processes illustrate the application of Le Chatelier's principle in the industry.

Haber Process for the Manufacture of Ammonia

In 1909 Fritz Haber established the conditions under which nitrogen, $N_2(g)$ and hydrogen, $H_2(g)$, would combine to give ammonia. This process produces ammonia with yield of approximately 10-20%. The Haber synthesis was developed into an industrial process by Carl Bosch.

The reaction between nitrogen gas and hydrogen gas to produce ammonia gas is an exothermic equilibrium reaction, releasing 92.4 kJ/mol of energy at 298K (25°C).

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{catalyst}]{\text{heat, pressure}} 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1} \qquad \ldots(1)$$

According to Le Chetalier's Principle:

- Increasing the pressure causes the equilibrium to move in the forward direction resulting in a higher yield of ammonia since there are more gas molecules on the left hand side of the equation (4 in total) than there are on the right hand side of the equation (1). Increasing the pressure means the system adjusts to reduce the effect of the change, that is, to reduce the pressure by having fewer gas molecules.
- Decreasing the temperature causes the equilibrium to move in the forward direction resulting in a higher yield of ammonia since the reaction is exothermic (releases heat). Reducing the temperature means the system will adjust to minimize the effect of the change, that is, it will produce more heat since energy is a product of the reaction, and will therefore produce more ammonia gas as well. However, the rate of the reaction at lower temperature is extremely slow, so a higher temperature must be used to speed up the reaction which results in a lower yield of ammonia.

The equilibrium expression for this reaction is:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

As the temperature increases, the equilibrium constant decreases and the yield of ammonia decreases.

Temperature (°C)	**K_{eq}**
25	6.4×10^{2}
200	4.4×10^{-1}
300	4.3×10^{-3}
400	1.6×10^{-4}
500	1.5×10^{-5}

Rate Considerations:

- The use of catalyst such as an iron, speeds up the reaction by lowering the activation energy so that the N_2 bonds and H_2 bonds can be more readily broken.
- Increased temperature means more reactant molecules have sufficient energy to overcome the energy barrier to reacting (activation energy) so the reaction is faster at higher temperatures (but the yield of ammonia is lower as discussed above). A temperature range of 400 – 500 °C is a compromise designed to achieve an acceptable yield of ammonia (10-20 %) within an acceptable time period.

At 200 °C and pressure above 750 atm there is an almost 100 % conversion of reactants to the ammonia product. Since there are difficulties associated with containing larger amounts of materials at such high pressure, lower pressure of around 200 atm are used industrially. By using a pressure of around 200 atm and a temperature of about 500 °C, the yield of ammonia is 10-20 %, while costs and safety concerns during operation of the plant are minimized.

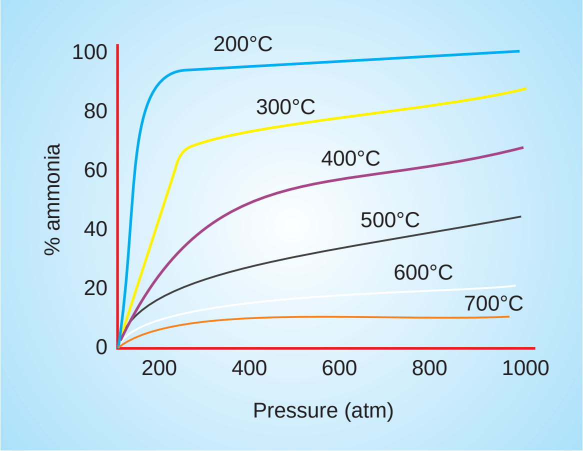


Figure 5.5 Effect of pressure on percentage yield of ammonia.

During industrial production of ammonia, the reaction never reaches equilibrium as the gas mixture leaving the reactor is cooled to liquefy and remove the ammonia. The remaining mixture of reactant gases is recycled through the reactor. The heat released by reaction is removed and used to heat the incoming gas mixture.

A flow diagram for the Haber process of manufacturing ammonia is shown below:

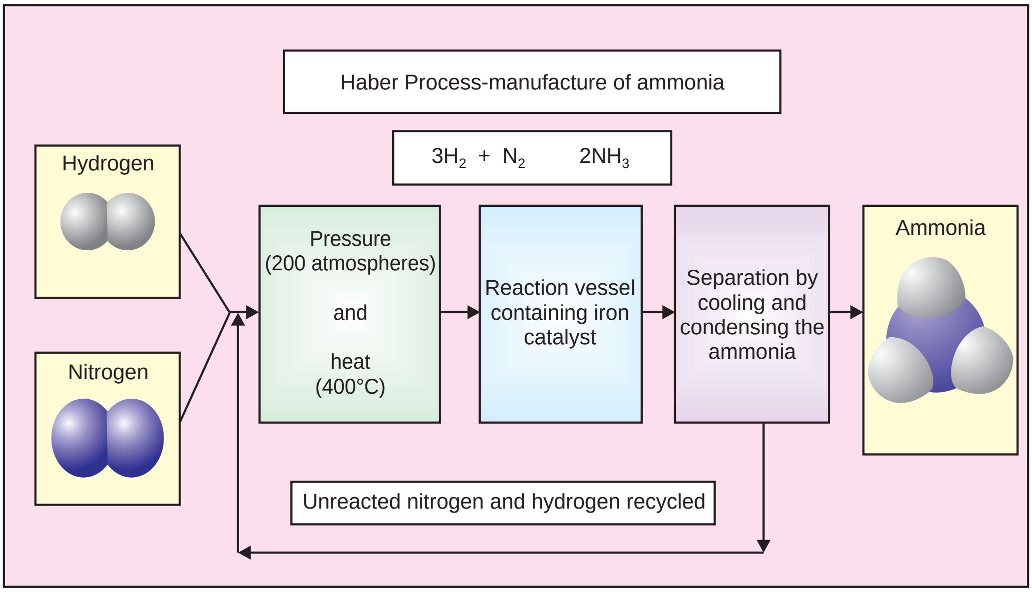


Figure 5.6 A flow scheme for Haber Process.

Contact Process for the Manufacture of Sulphuric acid

The manufacture of sulphuric acid by contact process involves the catalytic oxidation of sulphur dioxide SO_2 to sulphur trioxide SO_3, which is a reversible reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$$

Contact Process for Production of Sulphric Acid

Contact process involves the following steps:

(*i*) Solid sulphur, S(s), is burned in air to form sulphric dioxide gas, SO_2;

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

(*ii*) The gases are mixed with more air then cleaned by electrostatic precipitation to remove any particulate matter.

(*iii*) The mixture of sulphur dioxide and air is heated to 450 °C and subjected to a pressure of 101.3 - 202.6 kPa (1-2 atmospheres) in the presence of a vanadium catalyst (vanadium (V) oxide) to produce sulphur trioxide, $SO_3(g)$, with a yield of 98 %.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

(*iv*) Any unreacted gases from the above reaction are recylced back into the above reaction.

(*v*) Sulphur trioxide, $SO_3(g)$ is dissolved in 98 % (18 M) sulphuric acid, H_2SO_4, to produce disulphuric acid or pyrosulpuric acid, also known as fuming sulphuric acid or oleum, $H_2S_2O_7$.

$$SO_3(g) + H_2SO_4 \longrightarrow H_2S_2O_7$$

This is done because when water is added directly to sulphur trioxide to produce sulphuric acid,

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

the reaction is slow and tends to form a mist in which the reaction becomes very slow.

(*vi*) Water is added to the disulphuric acid, $H_2S_2O_7$, to produce sulphuric acid, H_2SO_4.

$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$$

The oxidation of sulphur dioxide to sulphur trioxide in step (*iii*) above is an exothermic reaction (energy is released), so according to Le Chatelier's Principle, higher temperatures will force the equilibrium position to shift to the left hand side of the equation favouring the production of sulphur dioxide. Lower temperatures would favour the production of the product sulphur trioxide and result in a higher yield. However, the rate of reaching equilibrium at the lower temperatures is extremely low. A higher temperature means equilibrium is established more rapidly but the yield of sulphur trioxide is lower. The temperature about 450°C is a compromising situation whereby a faster reaction rate results in a slightly lower yield.

Similarly, at higher pressures, the equilibrium position shifts to the equation in which there are the least numbers of gaseous molecules.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3$$

On the left hand side of the reaction there are 3 moles of gaseous reactants, and the right hand side are 2 moles of gaseous products, so higher pressure favours the right hand side, by Le Chatelier's Principle. Higher pressure results in a higher yield of sulphur trioxide. A vanadium catalyst (vanadium (V) oxide) is also used in this reaction to speed up the rate of the reaction.

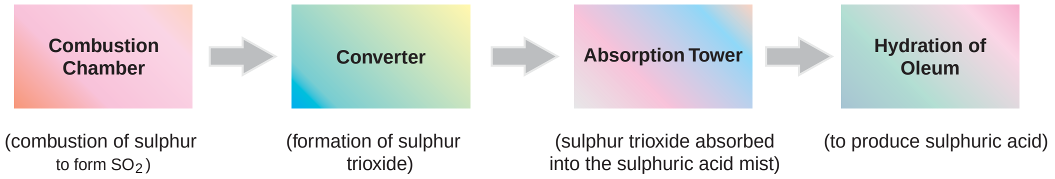


Figure 5.7 A flow scheme for Contact process.

Exercise 5.7

Answers the following questions:

1. Which compound is manufactured by Haber process?
2. What are the raw materials used in Haber process?
3. What is the role of iron in Haber process?
4. How are the reactions made to run faster in the Haber process?
5. Draw a flow chart to show what happens in the three stages of Haber process.
6. What is a mixture of H_2SO_4 and free SO_3?
7. What are the raw materials for making SO_2 in the contact process?
8. Why is SO_3 not directly added to make sulphuric acid?

5.2 PHASE EQUILIBRIUM

At the end of this section, you should be able to:

- explain the interplay between kinetic and potential energy that underlies the properties of the three states of matter and their phase changes;
- explain the process involved, both within a phase and through a phase change, when heat is added or removed from a pure substance;
- explain the meaning of vapour pressure and explain how phase changes are dynamic equilibrium processes;
- explain the relationship between vapour pressure and boiling point;
- describe how a phase diagram shows a phase of a substance at different conditions of pressure and temperature; and
- use a phase diagram to determine melting point, boiling point, critical temperature, critical pressure and triple point of a substance.

There are many physical processes that attain equilibrium under certain conditions. You have already performed an activity where equilibrium exists between ice and water. You also know that there are three states of matter, namely, solid, liquid and gas. Each substance can exist in any one state depending upon the temperature and pressure. A substance will exist in the gaseous state at high temperatures and low pressure. It will exist in solid state at low temperature and high pressure. In between the two conditions the substance will exist in the liquid state. These conditions are decided by the nature of the substance. At molecular level this can be interpreted in terms of forces of attraction and repulsion between the molecules.

5.2.1 Force of Attractions, Kinetic Energy and States of Matter

Activity 5.10

Form a group and perform the following activity:

In a test tube mix 1 mL of water with 1 mL of ethanol. Label it as A.

In another test tube take 1 mL of water and 1 mL of chloroform. Label it as B.

Discuss the following questions:

1. Find out in how many states the matter is present in test tubes A and B?
2. What is the difference between the liquids in the test tubes?

Share your ideas with the rest of the class.

In a substance the molecules are held together by the forces of attraction. At the same time each molecule possesses kinetic energy due to its motion. These two are opposing forces; forces of attraction bind the molecules together while kinetic energy tends to move the molecules apart.

- At very high temperatures, the molecules possess large kinetic energy, so

kinetic energy >> forces of attraction

As a result, molecules are far apart, the substance does not have definite shape or volume. This state is known as gaseous state.

- At very low temperatures, the molecules possess small kinetic energy, so

kinetic energy << forces of attraction

As a result, the molecules are held together strongly and the substance has definite shape and volume. This state is known as solid state.

- At intermediate temperatures the kinetic energy and forces of attraction match each other, that is,

kinetic energy ≈ forces of attraction

As a result, the molecules are held together, but not strongly, so that the substance has a definite volume but no definite shape. This state is known as liquid state.

5.2.2 Common terms: Phase, Component and Degree of Freedom

Phase: It is that part of the system which is physically and chemically homogeneous and separated from rest of the system by a discrete boundary. In this part the physical and chemical properties are uniform.

For some simple systems it is physically distinct part of the system that may be mechanically separated from other distinct parts.

The number of phases is represented by P. For example, a mixture of water and chloroform has two distinct layers, one of water and the other of chloroform (Activity 5.5). Therefore, there are two different phases although both are in the liquid state. Similarly, a mixture of two solids constitutes two different phases (Activity 5.6).

The simple rules for determining the number of phases are.

- Pure substance present in one state of matter constitutes one phase.
- Same substance present in different states of matter constitutes different phases. For example, ice and water are two different phases of H_2O.
- A mixture of gases constitutes one phase system.
- A homogeneous solution is a one phase system.
- For immiscible liquids, the number of layers formed is equal to the number of phases.
- For solids, each chemical species is a different phase. Different allotropic forms of the same substance constitute different phases. For example, diamond and graphite are different forms of carbon so they are different phases.

Component: It is the chemically distinct quantity present in the system. The number of components in a system is represented by C. When no chemical reaction takes place in the system, the number of components is equal to the total number of chemical species present in all the phases of the system. For example, an aqueous solution of sodium chloride has two components, $NaCl$ and water.

Degree of Freedom: It is the minimum number of variables required to describe each component in each phase of the system. It is represented by F. In the case of a pure substance present in one phase, the substance can be described completely if its temperature and pressure are known. For example, if you have H_2O and you also know its temperature and pressure, then you can predict all the properties, such as, whether it is in the solid, liquid or vapour state, as well as its density, refractive index, viscosity and other properties. Since only temperature and pressure are required to describe a pure substance, the degree of freedom of pure substance is 2.

Similarly, H_2O can coexist as ice and liquid water under specific conditions of temperature and pressures only. If the temperature is known then the pressure is fixed, similarly if the pressure is known the temperature is fixed. Since only one variable is required to completely describe a pure substance simultaneously present in two phases, its degree of freedom is two.

All the three states of matter of a substance coexist (present together) at a point known as triple point. The triple point has a fixed value of temperature and pressure and no variable is required to describe the system, so the degree of freedom is zero.

Example 5.8

1. Describe the number of phases present in the following systems:

   a Solution of sodium chloride in water.

   b A mixture of oil and water.

   c A mixture of hydrogen, oxygen and methane gases.

   d A mixture of powdered sodium chloride and potassium chloride.

   e Ice floating on water.

   Solution:

   a $P = 1$ since the solution is homogeneous.

   b $P = 2$ since oil and water are immiscible and they form two layers.

   c $P = 1$ since a mixture of gases is a homogeneous mixture.

   d $P = 2$ since NaCl and KCl are two different chemical species present in the solid state.

   e $P = 2$ since pure substance is present in two different states of matter.

2. Describe the number of components present in the following systems:

   a Solution of sodium chloride in water.

   b A mixture of hydrogen, oxygen and methane gases.

   c Ice floating on water.

   Solution:

   a $C = 2$ since two chemical species are present.

   b $C = 3$ since three chemical species, namely, hydrogen, oxygen and methane gas are present.

   c $C = 1$ since only one chemical substance, H_2O is present.

Exercise 5.8

Determine the number of phases and components that exist in each of the following systems:

a NH_4Cl solid is placed in an evacuated chamber. After a while, some ammonia and HCl appear in the gas phase above it.

b $COCl_2$, CO and Cl_2 at equilibrium with no excess of CO or Cl_2.

c $COCl_2$, CO and Cl_2 at equilibrium with excess of CO added (i.e., the concentrations of CO and Cl_2 are unequal).

5.2.3 Phase Rule

It is an important equation in the study of equilibrium between different phases in a system. It relates the number of phases and components to the degree of freedom by the following equation:

$$F = C - P + 2$$

This equation was given by Josiah William Gibbs, hence it is known as Gibbs Phase rule equation. This shows that the number of degrees of freedom (F) is equal to the number of components (C) minus the number of phases (P) plus the constant 2. The factor 2 stands for two parameters, namely, temperature and pressure.

Let us calculate the degree of freedom for one component system ($C = 1$). A simple example of one component is a pure substance. At a given time the pure substance can exist in one phase or more than one phases present together in equilibrium. The degree of freedom for various values of phases (1 – 4) can be calculated using the Phase rule equation.

For $P = 1$,

$F = 1 - 1 + 2 = 2$; such a system is known as bivariant system.

For $P = 2$,

$F = 1 - 2 + 2 = 1$; such a system is known as monovariant system.

For $P = 3$,

$F = 1 - 3 + 2 = 0$; such a system is known as invariant system.

For $P = 4$,

$F = 1 - 4 + 2 = -1$. This system is not possible as the degree of freedom can not be negative.

From this we can conclude that for one component system, at a given time, maximum of three phases can coexist in equilibrium.

Historical Note

Josiah Willard Gibbs

Josiah Willard Gibbs (1839 – 1903) was an American theoretical physicist, chemist and mathematician. He devised much of the theoretical foundation for both chemical thermodynamics and physical chemistry. He proposed Gibbs' phase rule, in the 1870s.

5.2.4 Temperature, Pressure and Phase Changes of Pure Substance

In this section, we will study how the phase of a pure substance changes when it is heated or cooled. The change in temperature may also be accompanied by the change in the pressure of system.

Changes Involved During Heating of the Pure Substance (one Component System)

When a pure substance is heated it undergoes various physical changes. These changes depend upon initial pressure at which the heating starts.

Activity 5.11

Form a group and perform the following activity:

Take 10 ice cubes in a beaker, dip a thermometer in it and start heating. Note the temperature and the physical changes taking place in the system.

Discuss the following questions in the group and afterwards share your ideas with rest of the class.

1. What happens when ice is heated?
2. Does the temperature change when the ice is melting?
3. How does the temperature vary when the ice has melted completely?
4. What will happen if water formed is further heated?

Reason for the Change in Phase on Heating

When a substance in the solid state is heated, the kinetic energy of its molecules increases and they start moving. At a higher temperature, the kinetic energy of the molecules becomes equal to the intermolecular forces of attraction, so these intermolecular forces start breaking and the liquid is formed. This temperature is known as melting point. On further heating the kinetic energy of the molecules goes on increasing and ultimately becomes much greater than the forces of attraction between the molecules. The molecules are able to overcome the forces of attraction and they start moving randomly. This is the stage when the substance gets converted into vapours.

Vapour Pressure and Boiling Point

When a liquid is taken in an evacuated closed vessel, some molecules at the surface of the liquid escape to the vapour phase. This happens when the kinetic energy of the surface molecules becomes greater than the intermolecular forces of attraction. This process is known as vapourization. As a result, the pressure inside the vessel starts increasing. When more and more molecules go from the liquid state to the vapour state, some molecules present in the vapour phase near the surface of the liquid go back to the liquid state. This process is known as condensation. The rate of condensation increases as more and more molecules go into the vapour phase. A stage comes when the rate of vapourzation becomes equal to the rate of condensation and dynamic equilibrium is attained. (Refer to Activity 5.3). The pressure exerted by the vapours at this stage is known as the vapour pressure of the liquid.

Vapour pressure is defined as the pressure exerted by the vapours in equilibrium with the liquid at a specific temperature.

As the temperature is increased, the kinetic energy of the molecules increases, so more molecules go from liquid phase to the vapour phase. As a result the total vapour pressure increases with the increase in temperature. When the vapour pressure becomes equal to the external pressure the liquid starts boiling. The temperature at which the vapour pressure of the liquid becomes equal to its external pressure is known as boiling point of the liquid. When the external pressure is equal to 1 atm, the boiling point is known as normal boiling point.

Exercise 5.9

Calculate the degree of freedom, F for each of the following:

1. An equilibrium gas phase containing N_2O_4 and NO_2.
2. Phosgene, CO and Cl_2 (with CO and Cl_2 derived from decomposition exclusively).
3. Phosgene, CO and Cl_2, with excess CO added.
4. NH_4Cl, initially in an evacuated chamber, with NH_3 and HCl present from decomposition.
5. Water, water vapor and ice in equilibrium.

5.2.5 Phase diagram

A Phase diagram is defined as a graphical representation the conditions when two or more phases (such as vapor-liquid, liquid-solid) of a system can exist in equilibrium.

Phase Diagram for one Component System

As we know one component system has only one chemical species (pure substance) and it can be described if the temperature and pressure of the system are known. Under specific conditions of temperature and pressure, the system can exist in one phase or two or three phases may be present in equilibrium. Phase diagram for a one component system is a graph which shows the variation of pressure of the system with temperature. It gives complete information about the conditions under which the different phases of the system are stable. It also gives the information about the temperature and pressure when the system changes from one phase to another phase.

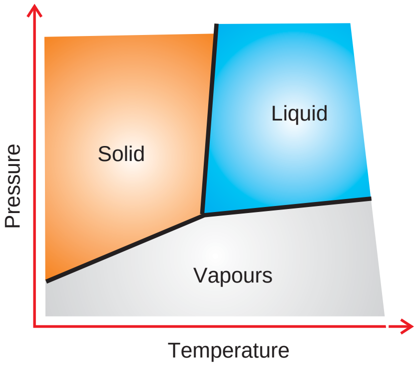


Fig. 5.8 Sketch of phase diagram of one component system.

Characteristics of a Phase Diagram for Pure Substance

- Temperature is plotted on *x*-axis and pressure on *y*-axis.
- The different regions of the graph represent different phases in which the substance can exist.
- A substance exists in solid state at low temperatures and high pressures. So the high pressure and low temperature region in the graph represents solid.
- A substance exists in vapour phase at high temperatures and low pressures, so this area in the graph represents vapour.
- The remaining area between the two regions represents liquid phase.
- The boundary between the phases is represented by a line. This line is obtained by joining the transition temperature between the two phases at different pressures. For example, the boundary between the solid and liquid phase represents points when solid changes to liquid or vice-versa. That is, it is the melting point temperatures at different pressures, so it is known as melting point curve. A boundary between liquid and vapour phase is known as vapourization curve. The solid and vapour phases are separated by sublimation curve.
- On transition line two phases are at equilibrium. For example, on melting line (OB) solid and liquid are in dynamic equilibrium. On boiling line (OC) liquid and its vapours are at equilibrium and at sublimation temperature, solid is in equilibrium with its vapours.
- The boundary line between two phases represents the two phase equilibria.
- The slope of the transition curves depends upon the nature of variation of transition temperature with pressure.
- A triple point represents three phases at equilibrium, i.e., at triple point all three phases coexist.

Phase Diagram of Pure Water

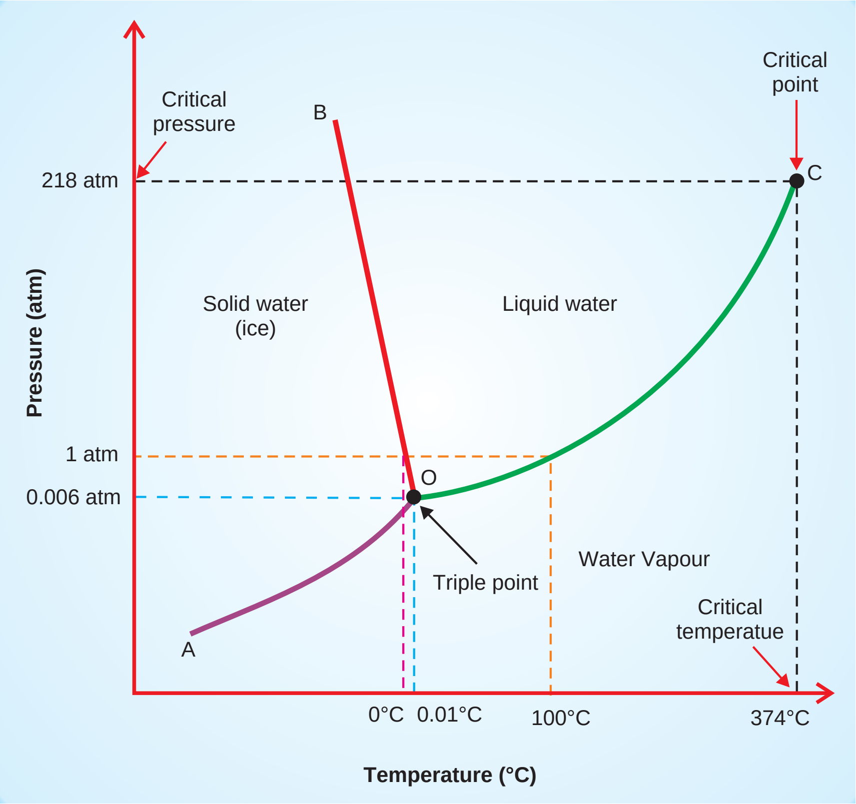


Fig. 5.9 Phase diagram of pure water.

The phase diagram for water shows three regions, namely, ice, liquid water and water vapour (Figure 5.6). Water is present in the form of ice at low temperatures and high pressures. So ice is represented by the region on the left of AOB. Water vapour is present at high temperatures and low pressures. So the region below AOC represents water vapour. Liquid water is present in the intermediate conditions. Therefore, it is represented by the region between BOC.

Curve AO is the boundary between ice and water vapour. On one side of the curve is the region representing ice; on the other side is the region representing water vapours. Along this curve, ice and vapours are present together at equilibrium, so it is known as sublimation curve. It gives the sublimation temperature of ice at different pressures. The slope of the curve is positive indicating that as the pressure increases, the sublimation temperature of ice also increases.

Curve OB represents the boundary between ice and liquid water. Along this curve water and ice exist in equilibrium, therefore it is known as fusion or melting curve. It represents the variation of melting point of ice at different temperatures. The slope of the curve is negative indicating that as the pressure is increasing the melting point of ice is decreasing.

Curve OC represents the boundary between water vapour and liquid water, therefore it is known as vapourization curve. It represents the variation of boiling point of water at different temperatures. The slope of the curve is positive indicating that as the pressure is increasing the boiling point of water is also increasing. This behaviour of decrease in melting point with increasing pressure is not common in the case of other substances. This special property is known as the anomalous behaviour of water.

At point O, ice, water and water vapour regions meet, so this point represents the triple point of water where all the three phases of water are at equilibrium. The temperature and pressure at triple point are 0.01°C and 0.006 atm respectively.

Point C represents critical point. At this temperature and pressure the meniscus between the liquid and the vapours disappears. Critical temperature is the maximum temperature at which the substance can exist in liquid state. The minimum pressure required to liquefy the vapours at critical temperature is known as critical pressure. For water the critical point lies at 374°C and 218 atm.

Exercise 5.10

Consider the phase diagram of pure water (Figure 5.9) and answer the following questions:

1. Under a pressure of 1 atmosphere, what is the maximum temperature at which the water can exist in liquid phase?
2. What will happen to ice if it is compressed at 0°C?
3. What is the point at which ice, liquid water and water vapour can coexist at equilibrium? Calculate the degree of freedom at this point.
4. The triple point of CO_2 is 518 kPa at – 56.6°C. Its critical point lies at 7.38 MPa at 31.1°C. The sublimation curve, fusion curve and vapourization curve have positive slope. Sketch the phase diagram of CO_2 and label it.

Applications of Phase Diagram

1. The phase diagram can be used to determine the phase of the system under the given conditions of temperature and pressure.
2. It can be used to determine the melting point, boiling point and sublimation temperature at different pressures.
3. Triple point and critical point can be determined from the phase diagram.
4. The changes taking place in a substance when it is heated at constant pressure can be predicted with the help of phase diagram.
5. The changes taking place in a substance when it is compressed at constant temperature can be predicted by phase diagram.

Unit Summary

- *A system is said to be at equilibrium when its macroscopic properties like temperature, pressure, concentration and energy do not change with time without any outside help.*
- *The equilibrium is dynamic in nature which means that although the macroscopic properties do not change, the processes do not stop at molecular level.*
- *Chemical equilibrium is the state of the reaction when the macroscopic properties like temperature, pressure, volume and concentration of the reaction do not change with time.*
- *According to the law of mass action the rate at which A and B combine is directly proportional to the product of their concentration terms each raised to the power of its respected coefficient in the balanced chemical reaction.*
- *For a general reaction at equilibrium* $aA + bB \rightleftharpoons mM + nN$ *the expression for* K_c *is*

$$K_c = \frac{[M]^m[N]^n}{[A]^a[B]^b}$$

- *The expression for* K_p *is*

$$K_p = \frac{[p_M]^m[p_N]^n}{[p_A]^a[p_B]^b}$$

provided that all A, B, M and N are in gaseous state.

- *The unit of* K_c *is* $(mol\ L^{-1})^{(m+n)-(a+b)}$ *and the unit of* K_p *is* $(atm)^{(m+n)-(a+b)}$
- $K_p = K_c(RT)^{\Delta n}$
- *When* $K_c > 1$ *the formation of products is favoured at equilibrium.*
- *When* $K_c < 1$*, So the formation of products is not favoured at equilibrium.*
- *When* $K_c = 1$*, it indicates that the reactants and the products are present in equal amounts.*
- *Reaction quotient is the ratio of concentrations of products to the concentrations of reactants raised to the power of their respective coefficients at any stage after the start of the reaction.*
- *For the reaction,* $aA + bB \rightleftharpoons mM + nN$ *the expression for the reaction quotient is*
- $Q = \dfrac{[M]^m[N]^n}{[A]^a[B]^b}$
- *When* $Q < K$*, then the reaction will proceed in the forward direction and more products will be formed till the equilibrium is reached.*
- *When* $Q > K$*, then the reaction will proceed in the reverse direction and more reactants will be formed till the equilibrium is reached.*
- *When* $Q = K$*, then the reaction has attained equilibrium.*
- *Le Chatelier's principle gives the effect of any one or more of the reaction parameters namely, temperature, pressure or concentration on equilibrium.*
- *For exothermic reactions the yield of products is increased by performing the reaction at lower temperatures.*
- *For endothermic reactions the yield of products is increased by performing the reaction at higher temperatures.*
- *When* $\Delta n > 0$ *the decrease in pressure favours the formation of products.*
- *When* $\Delta n < 0$ *the increase in pressure favours the formation of products.*

- *Removing the products from the reaction vessel shifts the reaction in the forward direction.*
- *Phase (P) is that part of the system which is physically and chemically homogeneous and separated from rest of the system by a discrete boundary.*
- *Component (C) is the chemically distinct quantity present in the system.*
- *Degree of freedom (F) is the minimum number of variables required to describe each component in each phase of the system.*
- *Gibbs Phase rule equation:* $F = C - P + 2$.
- *Vapour pressure is defined as the pressure exerted by vapours in equilibrium with the liquid at a given temperature.*
- *The temperature at which the vapour pressure of the liquid becomes equal to its external pressure is known as boiling point of the liquid.*
- *Phase diagram for a one component system is a graph which shows the variation of pressure with temperature. It gives the transition temperature between various phases.*

Check List

Key terms of the unit

- *Chemical equilibrium*
- *Components*
- *Critical point*
- *Critical temperature*
- *Degree of freedom*
- *Equilibrium constant*
- *Gibbs' phase rule*
- *Law of mass action*
- *Le Chateliers' principle*
- *Phase*
- *Phase diagram*
- *Phase equilibrium*
- *Reaction quotient*
- *Sublination curve*
- *Triple point*
- *Vaporization curve*

REVIEW EXERCISE

Part I: Multiple Choice Questions

1. Which of the following is correct about a reaction at equilibrium?

   a The concentrations of reactants and products are equal.

   b The system is static in nature.

   c The forward and backward rates are equal.

   d None.

2. For a reaction to shift towards the product direction, which of the following condition holds true?

   a $Q_c = K_c = 0$

   b $Q_c < K_c$

   c $Q_c > K_c$

   d $Q_c = K_c$

3. Given the equation $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$, the expression for K_c is:

   a $2[CO] / 2[C][O_2]$

   b $[CO]^2 / [C]^2[O_2]$

   c $[CO]^2 / [O_2]$

   d $2[CO] / [O_2]$

4. In which of the following cases does the reaction go farthest towards completion:

   a $K = 10^3$

   b $K = 10^{-2}$

   c $K = 10$

   d $K = 1$

5. For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are 2.0 atm and 4.0 atm, respectively, at equilibrium. What is the value of K_p for this reaction?

   a 0.5 atm

   b 4.0 atm

   c 8.0 atm

   d 32.0 atm

6. The equilibrium partial pressures of SO_2, O_2 and SO_3 are 0.1 atm, 0.25 atm and 0.5 atm respectively. The equilibrium constant for the reaction $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ is:

a 0.1

b 10

c 0.05

d 20

7. Which of the following is likely to happen when pressure is applied to the following system at equilibrium:

$$H_2O(s) \rightleftharpoons H_2O(l)$$

a More water will be formed

b More ice will be formed

c Water will evaporate

d No change occurs

8. The equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is K_1 and for the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ is K_2. The relation between K_1 and K_2 is:

a $K_1 = K_2$

b $K_1 = 1/K_2$

c $K_1 = -K_2$

d $K_1 = (K_2)^{0.5}$

9. What will happen when CaO is added to the following reaction at equilibrium?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

a No change occurs.

b Reaction shifts in the forward direction.

c More $CaCO_3$ is formed.

d Total pressure increases.

10. Under what conditions are K_p and K_c equal?

a $\Delta n = 1$

b $\Delta n = 0$

c $\Delta n = -1$

d They are never equal

Part II: Answer the following questions

11. For the reaction at equilibrium,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \quad \Delta H = -196 \text{ kJ mol}^{-1}$$

Predict the direction of the change on:

- a Removal of SO_2.
- b Addition of noble gas (argon) at constant pressure.
- c Decreasing volume of the system.
- d Increasing temperature of the system.
- e Addition of a catalyst.

12. Balance the following equations and write the equilibrium constant expressions, in terms of K_c and K_p.

- a $NH_3(g) + O_2(g) \rightleftharpoons N_2(g) + H_2O(g)$
- b $N_2(g) + H_2(g) \rightleftharpoons NH_3(g)$
- c $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

13. For the reaction at 200°C

$$2A(g) + B(g) \rightleftharpoons 3C(g)$$

the equilibrium constant is 3.0. Given the following information,

Species	**Concentration**
[A]	2.0 M
[B]	3.0 M
[C]	2.0 M

Predict the direction in which the reaction should proceed to reach equilibrium.

14. Given the reaction

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

what is the concentration of CO in equilibrium at 25°C in a sample of gas originally containing 1.00 mol L^{-1} of CO_2? For the dissociation of CO_2 at 25°C, $K_c = 2.96 \times 10^{-92}$.

15. A saturated solution of Na_2SO_4 with an excess of solid is present in equilibrium with its vapor in a closed vessel. Calculate the system's number of degrees of freedom. Also, identify the independent variables.

16. What happens to water when the pressure remains constant at 1 atm but the temperature changes from –10°C to 75°C? (refer to phase diagram for water)?

17. 5.0 moles of ammonia were introduced into a 5.0 L reaction chamber in which it partially decomposed at high temperatures;

$$2NH_3(g) \rightleftharpoons 3H_2(g) + N_2(g)$$

At equilibrium at a particular temperature, 80.0% of the ammonia had reacted. Calculate K_c for the reaction.

18. 1.25 mol NOCl was placed in a 2.50 L reaction chamber at 427°C. After equilibrium was reached, 1.10 moles of NOCl remained. Calculate the equilibrium constant K_c for the reaction.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

19. A sample of nitrosyl bromide was heated to 100°C in a 10.0 L container in order to partially decompose it.

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

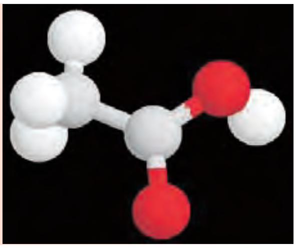
At equilibrium the container was found to contain 0.0585 mole of NOBr, 0.105 mole of NO, and 0.0524 mole of Br_2. Calculate the value of K_c.

20. The brown gas NO_2 and the colorless gas N_2O_4 exist in equilibrium.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

0.625 mole of N_2O_4 was introduced into a 5.00 L vessel and was allowed to decompose until it reached equilibrium with NO_2. The concentration of N_2O_4 at equilibrium was 0.0750 M. Calculate K_c for the reaction.

UNIT 6



Carboxylic Acids, Esters, Fats and Oils

Unit Outcomes

At the end of this unit, you should be able to:

- *write the structural formula and IUPAC names of given carboxylic acids and esters;*
- *describe some physical and chemical properties of carboxylic acids and esters;*
- *predict and correctly name the products of organic reactions, including substitution, addition, elimination, esterification, hydrolysis and oxidation reactions;*
- *carry out activities to prepare a carboxylic acid and an ester;*
- *list some important fatty acids;*
- *test for the carboxylic acid and ester functional groups;*
- *understand the structures, properties, uses of fats and oils;*
- *describe and explain reactions in soap making (saponification);*
- *describe and explain the cleaning action of soap and detergents;*
- *understand the harmful aspects of detergents on the environment when improperly disposed; and*
- *demonstrate scientific enquiry skills, including: observing, classifying, comparing and contrasting, asking questions, drawing conclusions, applying concepts and problem solving.*

MAIN CONTENTS

- Preparation of Carboxylic acids
- Fatty Acids
- Uses of Carboxylic acids

6.2 Esters
- Sources of Esters
- Structure and Nomenelature of Esters
- Physical Properties of Esters
- Chemical Properties of Esters
- Preparation of Esters
- Uses of Esters

6.3 Fats and oils
- Structure of Fats and Oils
- Physical Properties of Fats and Oils
- Hardening of oils
- Rancidity
- Soaps and Detergents

Start-up Activity

Form a group and perform the following activity:

Collect some common fresh fruits like banana, mango, grapes, apple, pineapple, etc. and some flowers from the garden. Observe the smell of all the fruits and flowers which you collected. Also taste the fruits and observe the sourness in each fruit. Now, discuss the following:

1. What type of odour (plseant or unplseant) do all the fruits and flowers have?
2. Do you find sourness and sweetness in all the fruits? If yes, then why do they have a different taste?

Share your ideas with the rest of the class.

INTRODUCTION

In Grade 10, you have studied about hydrocarbons and alcohols. In this unit, you will study about another important class of organic compounds called carboxylic acids and esters. These compounds are present in many fruits and flowers. Many carboxylic acids are used as food additives in jams, jellies, candies and pickels, etc. You will also study about fats and oils which are esters . Sodium or potassium salts of long chain fatty acids are called soaps which play a major role as cleansing agents.

6.1 CARBOXYLIC ACIDS

At the end of this section, you should be able to:

- list common organic acids and name their sources;
- write the general formula of saturated monocarboxylic acids;
- write the molecular formulas and names of the first six members of the saturated monocarboxylic acids;
- give the structural formula for the first four members of the saturated monocarboxylic acids;
- give the examples of mono, di and tricarboxylic acids;
- name some branched carboxylic acids;
- describe the physical properties of saturated monocarboxylic acids;
- explain the general methods of preparation of saturated monocarboxylic acids;
- explain the industrial and laboratory preparation of acetic acid;
- conduct an experiment to produce acetic acid in the laboratory;
- name and write structural formulas of some fatty acids; and
- describe some uses of common carboxylic acids.

6.1.1 Structure and Nomenclature of Carboxylic Acids

Activity 6.1

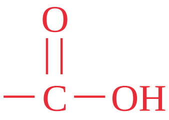
Recall your previous knowledge about hydrocarbons and alcohols in grade 10. Form a group and discuss the following:

1. Write the structures of first six alkanes and alcohols.
2. Compare the their strucutures.
3. Which functional groups in the structure determine the properties of these compounds?

Share your ideas with the rest of the class.

Structure of Carboxylic Acids

Carboxylic acids are organic compounds that contain at least one carboxyl group in their structure. A carboxyl group is a functional group consisting of a carbonyl and a hydroxyl which is usually written as —COOH or —CO_2H.

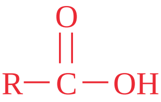


$$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Carboxyl group

a *Monocarboxylic acids*

The general formula for saturated monocarboxylic acids can be written as:

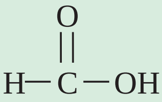


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

where R is either hydrogen or an alkyl group for aliphatic Carboxylic acids. When R is phenyl (aryl) group, the structure represents aromatic carboxylic acids.

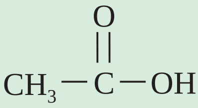
Example 6.1

1. The structure of the first three saturated monocarboxylic acids are written as follows:

a 

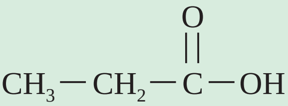
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Methanoic acid

b 

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

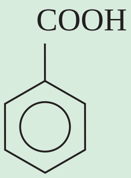
Ethanoic acid

c 

$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Propanoic acid

2. The simplest aromatic carboxylic acid is benzoic acid. Its structure is written as:



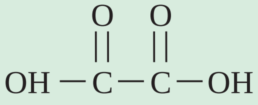
Benzene carboxylic acid (Benzoic acid)

b *Di- and tricarboxylic acids*

Carboxylic acids containing two carboxyl groups in their structure are called dicarboxylic acids.

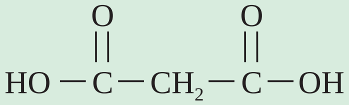
Example 6.2

1. The structure of the first three saturated dicarboxylic acids are written as follows:

a 

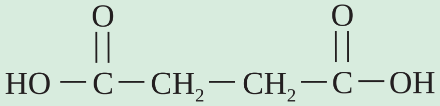
$$\mathrm{OH-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH}$$

Ethanedioic acid

b 

$$\mathrm{HO-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OH}$$

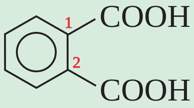
Propanedioic acid

c 

$$\mathrm{HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH}$$

Butanedioic acid

2. The simplest aromatic dicarboxylic acid is phthalic acid. Its structure is:

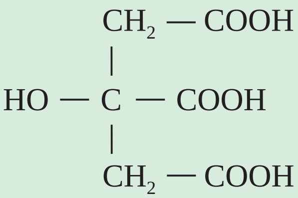


1, 2-Benzenedicaboxylic acid (phthalic acid)

Similarly, carboxylic acids that contain three carboxyl groups in their structure are called tricarboxylic acids.

Example 6.3

Citric acid is a typical tricarboxylic acid, having the following structure:



$$\begin{array}{rcl} & \mathrm{CH_2} & \mathrm{-\,COOH} \\ & | & \\ \mathrm{HO\,-} & \mathrm{C} & \mathrm{-\,COOH} \\ & | & \\ & \mathrm{CH_2} & \mathrm{-\,COOH} \end{array}$$

Citric acid

Activity 6.2

Form a group and make a list of some fruits having acidic taste. Try to identify the carboxylic acids present in these fruits, and classify these acids as monocarboxylic, dicarboxylic, and tricarboxylic acids.

Present your findings to the class.

Exercise 6.1

1. Write the structure of the following monocarboxylic acids:
   - a Butanoic acid
   - b Pentanoic acid
2. Write the structure of the following dicarboxylic acids:
   - a Pentanedioic acid
   - b Hexanedioic acid
   - c 1,3-Benzenedicarboxylic acid

Nomenclature of Carboxylic Acids

i Common names carboxlic acids

a Straight chain monocarboxylic acids

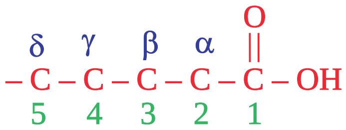
A large number of carboxylic acids have widely used common names which need to be learned. Those with an even number of carbon atoms ranging from 4 to 22 may be obtained by hydrolysis of animal and vegetable fats and oils. They are referred to as fatty acids, and they have common names derived from various sources. Formic acid derives its name from the Latin word for ants, because it is one of the toxic ingredients of the secretion injected by the stinging ant. Butanoic acid (butyric acid) derives its name from butter, in which it is found when the butter becomes rancid. Caproic, caprylic, and capric acids are involved in the odor of a goat, and their names derive from the Latin word, caper, for goat. Table 6.1 lists common names of some of the most important monocarboxylic acids.

Table 6.1 Common names of some monocarboxylic acids

Structure	Common name	Source of name
HCOOH	Formic acid	Ant (Latin, formica)
CH_3-COOH	Acetic acid	Vinegar (Latin, acetum)
CH_3-CH_2-COOH	Propionic acid	Milk (Greek, propion)
$CH_3-CH_2-CH_2-COOH$	Butyric acid	Butter (Latin, butyrum)
$CH_3-CH_2-CH_2-CH_2-COOH$	Caproic acid	Goat (Latin, caper)

b Branched chain and substituted carboxylic acids

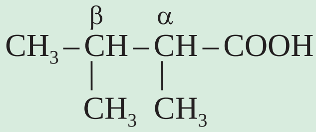
In common naming system, the branched chain and substituted acids are named as derivatives of straight chain carboxylic acids. In this case, the position of the side chain or substituents is indicated by Greek letters, α, β, γ, δ... for designating the 1st, 2nd, 3rd,… position of carbon atoms as shown below:



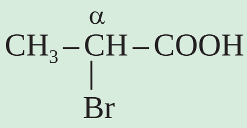
$$-\underset{5}{\overset{\delta}{C}}-\underset{4}{\overset{\gamma}{C}}-\underset{3}{\overset{\beta}{C}}-\underset{2}{\overset{\alpha}{C}}-\underset{1}{\overset{\overset{O}{\|}}{C}}-OH$$

Example 6.4

Write the common names for:

a 

$$\overset{\beta}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}}-\overset{\alpha}{\underset{\displaystyle CH_3}{\underset{|}{CH}}}-COOH$$

b 

$$CH_3-\overset{\alpha}{\underset{\displaystyle Br}{\underset{|}{CH}}}-COOH$$

Solution:

a It is monocaroxylic acid that consists of four carbon atoms. So, it is common name is butyric acid. In addition to this, two methyl groups are attached to α-and β-positon carbon atoms in the structure. Now, the complete common name is α, β-dimethylbutyric acid.

b Similarly, the given acid contains three carbon atoms. Hence, the common name is propionic acid. Next, the position of bromo group , which is attached to α-carbon atom in the structure. This gives the complete common name as α-bromopropionic acid.

c *Dicarboxylic acids*

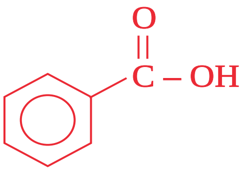
Dicarboxylic acids also possess common names which are based on their sources. Table 6.2 lists common names of some of the most important dicarboxylic acids.

Table 6.2 Common names of some dicarboxylic acids

Structure	Common name
HOOC–COOH	Oxalic acid
$HOOC-CH_2-COOH$	Malonic acid
$HOOC-CH_2-CH_2-COOH$	Succinic acid
$HOOC-CH_2-CH_2-CH_2-COOH$	Glutaric acid
$HOOC-CH_2-CH_2-CH_2-CH_2-COOH$	Adipic acid
$HOOC-CH_2-CH_2-CH_2-CH_2-CH_2-COOH$	Pimelic acid

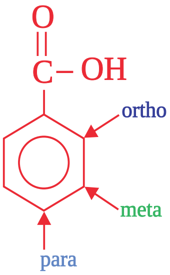
d *Aromatic carboxylic acids*

Compounds which have a carboxyl group directly attached to an aromatic ring are classified as aromatic carboxylic acids. The simplest aromatic carboxylic acid has a carboxyl group attached to benzene ring and its common name is benzoic acid.



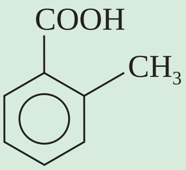
Benzoic acid

In common naming system, the name of substituted aromatic acids are written by prefixing the names of substitutes. The position of the substituent is indicated by the prefixes ortho (o-), meta (m-), para (p-) as it is shown in the structure below.



Example 6.5

1. Write the common name for:



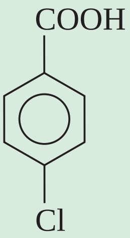
Solution:

Since the methyl group is attached to ortho- position, then the IUPAC name becomes *o*-methylbenzoic acid.

2. Write the structure for *p*-chlorobenzoic acid.

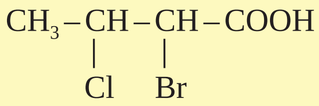
Solution:

The structure of benzoic acid with chloro group attached to *para* position is:



Exercise 6.2

1. Write the common names for the following carboxylic acids:

a 

$$\mathrm{CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH}}-COOH}$$

b $COOH - CH_2 - CH_2 - COOH$

2. Write the structures of carboxylic acids from the given common names:

a Acetic acid b Ethanedioic acid c β-Bromobutyric acid

ii IUPAC names of carboxlic acids

a Straight chain monocarboxylic acid

According to IPUAC system, monocarboxylic acids are named as alkanoic acids. The longest chain of carbon atoms containing the carboxyl group is selected and the name is derived from the corresponding alkane by replacing the suffix "–e" with "–oic acid".

Example 6.6

1. Write the IPUAC names for:

a $H–COOH$ b $CH_3–COOH$

Solution:

a The longest chain contains only one carbon atom. The corresponding alkane name is methane. Now, we drop the suffix "–e" and replace it by "–oic acid" so, the complete IPUAC name becomes methanoic acid.

$H–COOH$	Methanoic acid

b Similarly, the longest chain in the structure is derived form and alkane with two carbon atoms called ethane. Now, when we drop the suffix "–e" and replace it with "–oic" acid, we get the complete IPUAC name of ethanoic acid.

$CH_3–COOH$	Ethanoic acid

2. Write the structure of

a Propanoic acid b Butanoic acid

Solution:

a Monocarboxylic acid with three carbon atoms is called propanoic acid.

$CH_3–CH_2–COOH$ Propanoic acid

b Butanoic acid is IPUAC name given to moncarboxylic acid with four carbon atoms.

$CH_3–CH_2–CH_2–COOH$ Butanoic acid

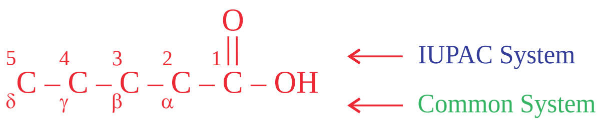
Table 6.3 lists IUPAC names for the first six monocarboxylic acids.

Table 6.3 IUPAC names of some monocarboxylic acids

Structure	IUPAC Name
HCOOH	Methanoic acid
CH_3COOH	Ethanoic acid
CH_3CH_2COOH	Propanoic acid
$CH_3(CH_2)_2COOH$	Butanoic acid
$CH_3(CH_2)_3COOH$	Pentanoic acid
$CH_3(CH_2)_4COOH$	Hexanoic acid

b Branched chain and substituted monocarboxylic acids

In IUPAC system, the positions of the substitutes are indicated by Arabic numerals as 1, 2, 3. The numbering of the chain starts from the carboxyl carbon and it is alwasy assigned C-1 position. Note that C-2 position in the IUPAC system corresponds to the α-position in the common naming system.



$$\underset{\delta}{\overset{5}{C}}-\underset{\gamma}{\overset{4}{C}}-\underset{\beta}{\overset{3}{C}}-\underset{\alpha}{\overset{2}{C}}-\overset{O}{\overset{\|}{\overset{1}{C}}}-OH$$

Example 6.7

1. Write the IUPAC names for:

a $CH_3–CH(CH_3)–COOH$ b $CH_3–CH(Cl)–CH(CH_3)–COOH$

Solution:

a The carboxylic acid given contains three carbon atoms which makes IUPAC name to be propanoic acid. There is also methyl group attached to the 2nd carbon atom, so the substituent is 2-methyl. Thus, the complete IUPAC name is 2-methylpropanoic acid.

$CH_3–CH(CH_3)–COOH$ 2-Methylpropanoic acid

b The longest chain in the structure consists of four carbon atoms and this gives IUPAC name of butanoic acid. The chloro group (–Cl) is attached to the 3rd carbon atom and the methyl group is located at the 2nd carbon atom. Based on the alphabetical order, these substituents are arranged as 3-chloro-2-methyl. Finally, the complete IUPAC name of this acid becomes 3-chloro-2-methyl butanoic acid.

$CH_3–CH(Cl)–CH(CH_3)–COOH$ 3-Chloro-2-Methylbutanoic acid

c Dicarboxylic acids

In IUPAC system, dicarboxylic acids are named as alkanedioic acids. These names are obtained by replacing the suffix "–e" in the name of corresponding alkane by "–dioic acid".

Example 6.8

1. Write the IUPAC name for:

$HOOC–CH_2–CH_2–COOH$

Solution:

This dicarboxylic acid contains four carbon atoms. The name of the corresponding alkane is butane. Now, the suffix "–e" is replaced by "–dioic acid". This gives the complete IUPAC name of butanedioic acid.

$HOOC–CH_2–CH_2–COOH$ Butanedioic acid

2. Write the structure of propanedioic acid.

Propanedioic acid refers to IUPAC name of dicarboxylic acid that contains three carbon atoms. Hence, the structure is written as shown below:

$HOOC–CH_2–COOH$ Propanedioic acid

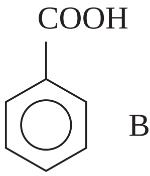
Table 6.4 lists the IUPAC names of the first six dicarboxylic acids.

Table 6.4 IUPAC names of dicarboxylic acids

Structure	IUPAC Name
HOOC - COOH	Ethanedioic acid
HOOC - CH_2- COOH	Propane dioic acid
HOOC - $(CH_2)_2$ - COOH	Butane dioic acid
HOOC - $(CH_2)_3$ - COOH	Pentane dioic acid
HOOC - $(CH_2)_4$ - COOH	Hexane dioic acid
HOOC - $(CH_2)_5$ - COOH	Heptanes dioic acid

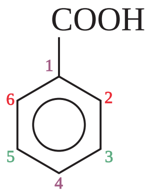
d *Aromatic carboxylic acids*

According to IUPAC system, aromatic carboxylic acids are named as benzenecarboxylic acids.



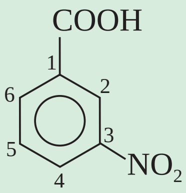
Benzenecarboxylic acid

The position of the substitutes is indicated by the Arabic numerals 1, 2, 3,...starting with aromatic carbon bearing carboxyl group as C–1 and it is shown in the structure below.



Example 6.9

1. Write the IUPAC name for:

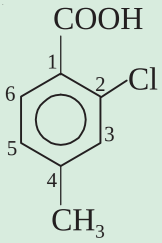


Solution:

1. The nitro group (–NO_2) is attached to the 3rd carbon of the aromatic ring. Hence, the complete IUPAC name becomes 3-nitrobenzenecarboxylic acid.
2. Write the structure for 2-chloro-4-methylbenzenecarboxylic acid.

Solution:

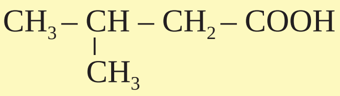
We have two substituents, chloro group (–Cl) attached to the 2nd carbon atom and methyl group (–CH_3) to the 4th carbon atom. So, the structure of this aromatic carboxylic acid is:



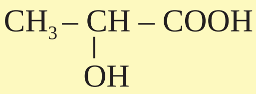
2-Chloro-4-methylbenzene carboxylic acid

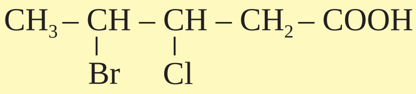
Exercise 6.3

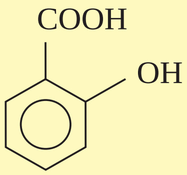
1. Write the IUPAC names for the following carboxylic acids:

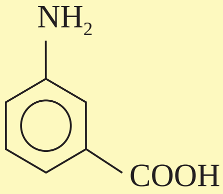
a

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COOH$

b
$Br-CH_2-CH_2-CH_2-CH_2-COOH$

c

$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH$

d

$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-COOH$

e 

f 

2. Draw the structures of the following carboxylic acids:

a 2, 3-Dichloropropanoic acid

b 4-Methylbenzoic acid

c 2-Fluorobutanoic acid

d 4-Hydroxy-2-bromobenzoic acid.

6.1.2 Physical Properties of Carboxylic Acids

Activity 6.3

Form a group and discuss the following:

1. The solubility of monocarboxylic acids in water decreases with increase in molecular mass.
2. The higher monocarboxylic acids are almost odourless.
3. Should the alcohols possess higher or lower boiling points than that of monocarboxylic acids of comparable molar masses?

Share your ideas with the class.

1. *State*

The lower aliphatic acids containing up to 9 carbon atoms are liquids, whereas the higher members are colourless waxy solids. Benzoic acid and most of its derivatives are also colourless solids.

2. *Odour*

The odours of the lower aliphatic acids progress from sharp, irritating odour of methanoic acid and ethanoic acids to the distinctly unpleasant odour of the butanoic, pentanoic and hexanoic acids. The higher acids have little odour because of their low volatility.

3. *Boiling Point*

Carboxylic acids have higher boiling points than alcohols of the similar size. For example, ethanoic acid (CH_3COOH) boils at 118°C while the alcohol of comparable molecular mass, propan-1-ol ($CH_3CH_2CH_2OH$) boils at 97.2°C. The higher boiling points of the carboxylic acids are also caused by hydrogen bonding between two molecules of acid to produce a dimer. The –OH and $>C=O$ groups of one acid molecule form hydrogen bonding with $>C=O$ and –OH groups of another molecule. Figure 6.1 shows the structure of two carboxylic acids with two intermolecular H-bonds between them.

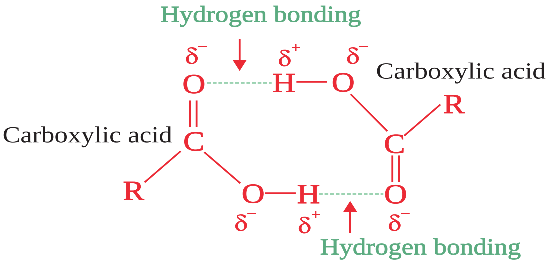


Figure 6.1 Carboxylic acid dimer.

The formation of a dimer immedately doubles the size of the molecule and so increases the Van der Waals dispersion forces between one of these dimers and its neighbours resulting in a high boiling point.

4. *Solubility*

In the presence of water, the carboxylic acids do not dimerize. Instead, hydrogen bonds are formed between water molecules and individual molecules of acid. Carboxylic acids up to four carbon atoms mix well with water in any proportion. The solubility in water decreases with the increasing molecular mass and higher acids are almost insoluble. The carboxylic acids dissolve in water due to formation of hydrogen bonding with water molecules. The higher carboxylic acids are insoluble in water because of the decrease in the hydrogen bonding with water molecules as hydrocarbon increases (Figure 6.2).

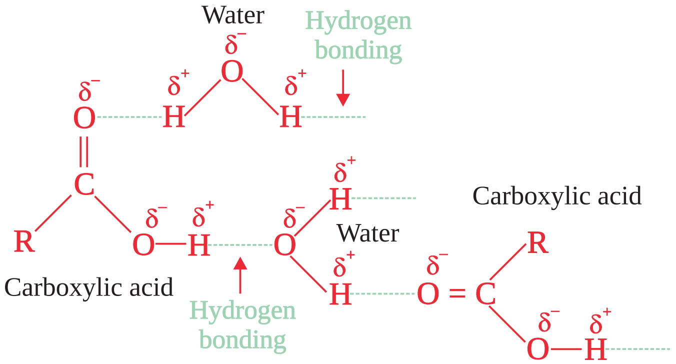


Figure 6.2 Formation of hydrogen bonding between carboxylic acids and water molecules.

Among the aromatic acids, benzoic acid is sparingly soluble in water at room temperature, although the solubility is more in hot water. However, all carboxylic acids are soluble in organic solvents like alcohol, ether, benzene etc.

The boiling points, melting points and solubilities of some carboxylic acids are given in Table 6.5.

Table 6.5 Physical constants of some carboxylic acids

Structure	IUPAC Name	Boiling point °C	Solubility, g/100 mL H_2O at 25°C
$HCOOH$	Methanoic acid	100.5	∞*
CH_3COOH	Ethanoic acid	118	∞*
CH_3CH_2COOH	Propanoic acid	141	∞*
$CH_3(CH_2)_2COOH$	Butanoic acid	164	∞*
$CH_3(CH_2)_3COOH$	Pentanoic acid	187	4.97
$CH_3(CH_2)_4COOH$	Hexanoic acid	205	1.08
$CH_3(CH_2)_5COOH$	Heptanoic acid	223	—
$CH_3(CH_2)_6COOH$	Octanoic acid	239	0.07
$CH_3(CH_2)_7COOH$	Nonanoic acid	253	—
$CH_3(CH_2)_8COOH$	Decanoic acid	269	0.015

∞* means miscible in all proportions.

Exercise 6.4

1. Arrange the following aliphatic carboxylic acids in the decreasing order of boiling point:

a butanoic acid
c octanoic acid
b decanoic acid
d propanoic acid

2. Which aliphatic carboxylic acid is most soluble in water?

   a heptanoic acid
   c ethanoic acid
   b hexanoic acid
   d pentanoic acid

3. Which aliphatic carboxylic acid has the lowest boiling point?

   a pentanoic acid
   c hexanoic acid
   b methanoic acid
   d propanoic acid

4. Arrange in order of increasing boiling point:

   a C_5H_{12}
   Pentane
   c $C_4H_{11}OH$
   Butanol
   b C_2H_5COOH
   Propanoic acid
   d $CH_3(CH_2)_4COOH$
   Hexanoic acid

6.1.3 Chemical Properties of Carboxylic Acids

Activity 6.4

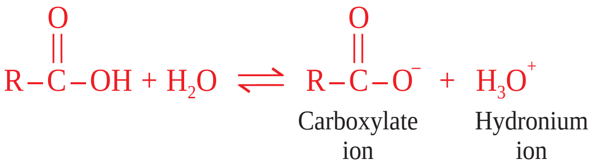
Form a group and perform the following:

Take 400 mL beaker and fill it with water to 2/3 level. Add 2 spoons of sodium bicarbonate and dissolve it. Then add few drops of litmus solution and 4-5 naphthalene balls. Now add benzoic acid, a pinch at a time and observe carefully. Explain the observations and discuss in the class.

The carboxylic acids show reactions due to the alkyl or aryl group and the carboxyl group. The carboxyl group is further considered to be made up of a carbonyl and a hydroxyl group. All these groups modify the properties of each other due to their interaction. Some of the common reactions of carboxylic acids are:

i) Reaction as an acid

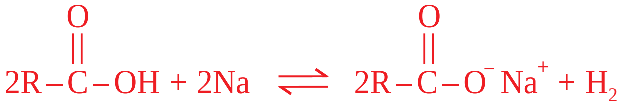
In aqueous solution, the cleavage of O–H bond occurs leading to the formation of carboxylate ion and hydronium ion. Carboxylic acids ionize partially and an equilibrium exists between the ionized and un-ionized forms.



$$R-\overset{\overset{O}{\parallel}}{C}-OH + H_2O \rightleftharpoons \underset{\text{Carboxylate ion}}{R-\overset{\overset{O}{\parallel}}{C}-O^-} + \underset{\text{Hydronium ion}}{H_3O^+}$$

Carboxylic acids are weak acids and dissociates slightly. The following are examples of reactions of carboxylic acids as an acid.

a Reaction with metals : Carboxylic acids react with active metals *such as* Na, K, Mg, Ca etc. to form salts and hydrogen gas.



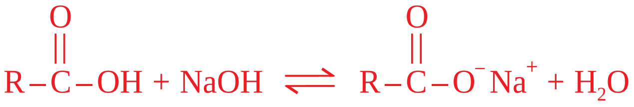
$$2R-\overset{\overset{O}{\parallel}}{C}-OH + 2Na \rightleftharpoons 2R-\overset{\overset{O}{\parallel}}{C}-O^-Na^+ + H_2$$

The salts of carboxylic acids are named by writing the name of the metal first, followed by the name of the acid replacing the ending -ic acid by -ate.

For example, sodium reacts with ethanoic acid to form sodium ethanoate and hydrogen.

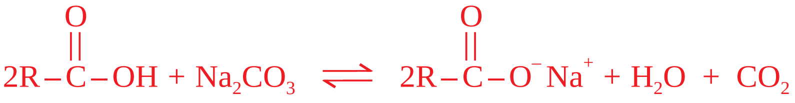
$$2CH_3-COOH + 2Na \rightarrow 2CH_3-COO^-Na^+ + H_2$$

b Reaction with Bases : Carboxylic acids react with strong bases like sodium hydroxide or potassium hydroxide to form the corresponding salts and water.

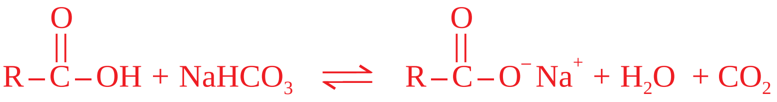


$$R-\overset{\overset{O}{\parallel}}{C}-OH + NaOH \rightleftharpoons R-\overset{\overset{O}{\parallel}}{C}-O^-Na^+ + H_2O$$

Reaction with base is a simple neutralization reaction. Carboxylic acids react with weak bases like carbonates or bicarbonates to form salt, water and carbon dioxide.

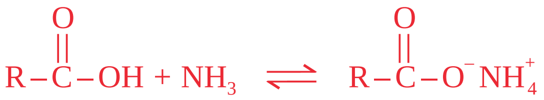


$$2R-\overset{\overset{O}{\parallel}}{C}-OH + Na_2CO_3 \rightleftharpoons 2R-\overset{\overset{O}{\parallel}}{C}-O^-Na^+ + H_2O + CO_2$$



$$R-\overset{\overset{O}{\parallel}}{C}-OH + NaHCO_3 \rightleftharpoons R-\overset{\overset{O}{\parallel}}{C}-O^-Na^+ + H_2O + CO_2$$

They also react with ammonia to form ammonium salts of carboxylic acids.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3 \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-NH_4^+$$

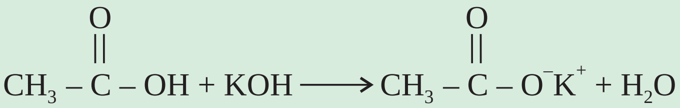
Example 6.10

Write the chemical equations for the reaction between ethanoic acid and each of the following reagents and write the names of the products formed:

a KOH   b Na_2CO_3 c NH_3

Solution:

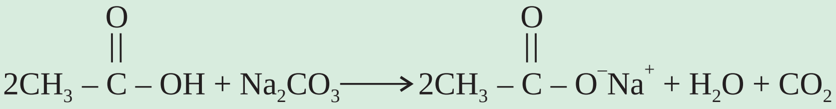
a



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + KOH \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^-K^+ + H_2O$$

Potassium ethanoate

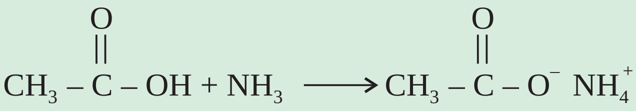
b



$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + Na_2CO_3 \longrightarrow 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + H_2O + CO_2$$

Sodium ethanoate

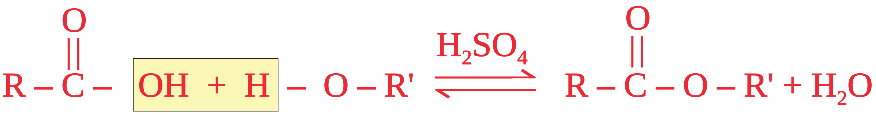
c



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^-\ NH_4^+$$

Ammonium ethanoate

ii) Formation of Esters : One of the important reactions of carboxylic acids involves the replacement of –OH group by an alkoxy group to form esters as products. In this reaction, carboxylic acids are heated with alcohols in the presence of concentrated sulphuric acid. The reaction is called esterification.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{OH + H}-O-R' \xrightleftharpoons{H_2SO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O$$

Carboxylic acid   Alcohol   Ester

Activity 6.5

Form a group and discuss the reason why 'tella' or 'tej' turn sour when kept for longer time?

After the discussion, share your ideas with the rest of the class.

6.1.4 Preparation of Carboxylic Acids

One of the important methods for preparation of carboxylic acids is oxidation. Many saturated monocarboxylic acids are obtained by the oxidation of the corresponding primary alcohols whereas aromatic acids are obtained from the corresponding alkylbenzenes.

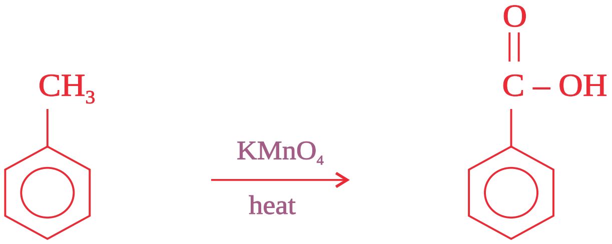
i) Oxidation of Primary Alcohols: The primary alcohols are readily oxidized to the corresponding carboxylic acids by their reaction with common oxidizing agents like potassium permanganate or potassium dichromate. The oxidation can also be carried out by passing the vapours of primary alcohols through copper (II) oxide.

$$R-CH_2-OH \xrightarrow{KMnO_4} R-\overset{\overset{\displaystyle O}{||}}{C}-OH$$

For example, oxidation of ethanol yields acetic acid (ethanoic acid).

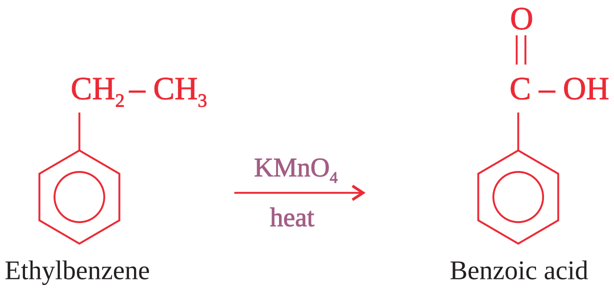
$$CH_3-CH_2-OH \xrightarrow{KMnO_4} CH_3-\overset{\overset{\displaystyle O}{||}}{C}-OH$$

ii) Oxidation of Alkylbenzenes: Aromatic compounds containing alkyl group as substituent undergo oxidation to form aromatic acids. The reaction involves oxidation with potassium permanaganate or potassium dichromate under vigorous conditions. The alkyl group is oxidised to carboxyl group irrespective of its size. For example, toluene and ethylbenzene, both give benzoic acid on refluxing with $KMnO_4$ in alkaline medium.



Toluene

Benzoic acid



iii) Preparation of acetic acid (Ethanoic acid) : Acetic acid is one of the important carboxylic acids which is used as food preservative. It can be prepared in laboratory by the oxidation of ethanol with potassium permanganate. It can also be obtained by passing the vapours of ethanol through copper oxide as described in Experiment 6.1.

Experiment 6.1

Laboratory Preparation of Acetic Acid

Objective: To prepare acetic acid in the laboratory by oxidation of ethanol.

Apparatus: Goggles, test tubes, test tube rack, quickfit apparatus, 250 mL beaker, pipettes, Bunsen burner, stand, clamp, tripod, wire gauze, digital balance, blue litmus paper, broken porcelain pieces.

Chemicals: Ethanol, sodium dichromate, 1 M sulphuric acid, 0.5 M sodium carbonate solution, blue litmus paper.

Procedure

Oxidation of ethanol to ethanoic acid

1. Set up the Quickfit apparatus for refluxing as shown in Figure 6.3.
2. Place about 10 mL of 1 M sulphuric acid into the 250 mL round-bottom flask.
3. Add 2-3 g of sodium dichromate ($Na_2Cr_2O_7$) and a few pieces of broken porcelain. Swirl the contents of the flask until the solution is complete (warm if necessary).
4. Cool the mixture under a running tap.
5. Add 1 mL of ethanol dropwise into the flask.
6. Boil under reflux for 20 minutes and distil 2-3 mL of the liquid.

7. Notice the smell of the product (distilled liquid) and compare it with that of ethanol.
8. Add a few drops of the distilled liquid to a small amount of solid sodium carbonate.
9. Add a drop of the distilled liquid to moistened blue litmus paper.

Observation and analysis

1. What happened to the colour of the solution in the flask?
2. What is the role of sodium dichromate in the above reaction? Is it oxidized or reduced?
3. Write the chemical equation for this reaction.
4. What do you conclude from this experiment?

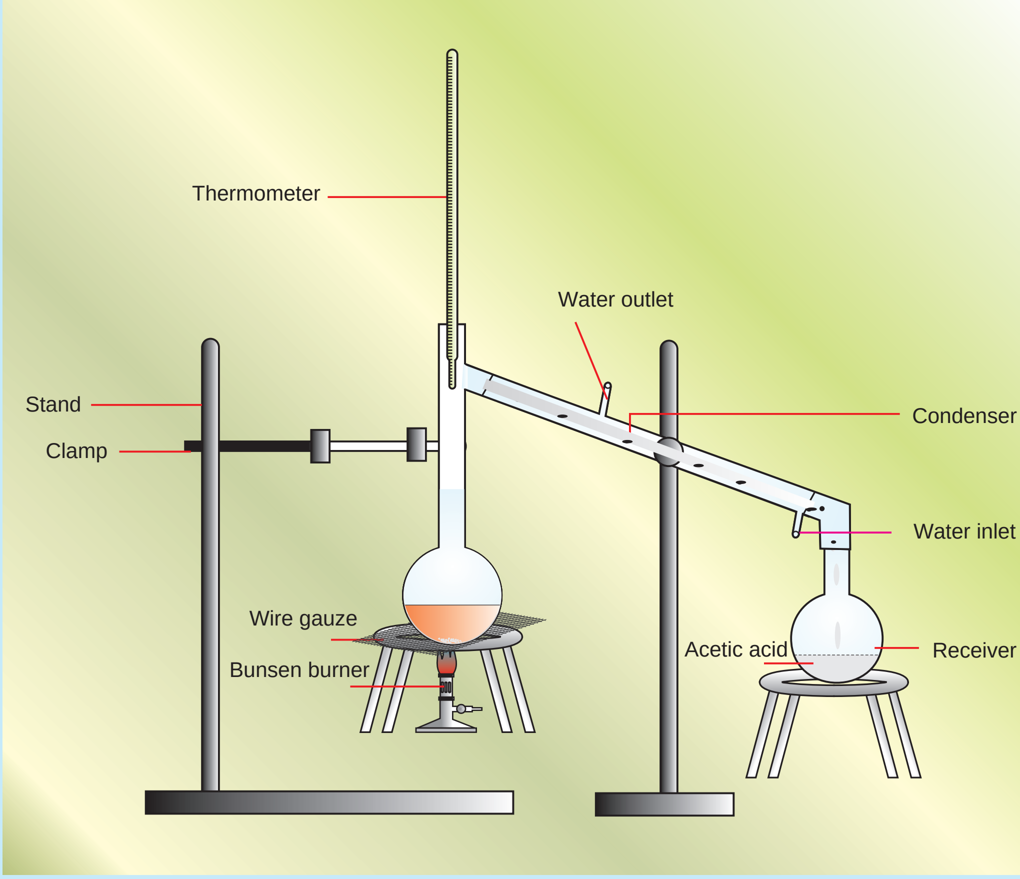


Figure 6.3 **Laboratory setup for preparation of acetic acid.**

Large quantities of acetic acid is obtained in industry from fermentation of ethanol. The process is known as Quick Vinegar Fermentation Process. In the process large wooden vats (Figure 6.4) are used which have a perforated bottom. They are packed with wood shavings moistened with old vinegar. Ethanol solution is poured from the top and trickles down slowly to the perforated bottom. From the lower portion, air is pumped in the vat. The bacteria present in old vinegar, ferment the ethanol into acetic acid. The liquor obtained at the bottom is recirculated through the tower. The maximum concentration of acetic acid obtained by this process is about 10%, which can be fractionated to yield glacial acetic acid.

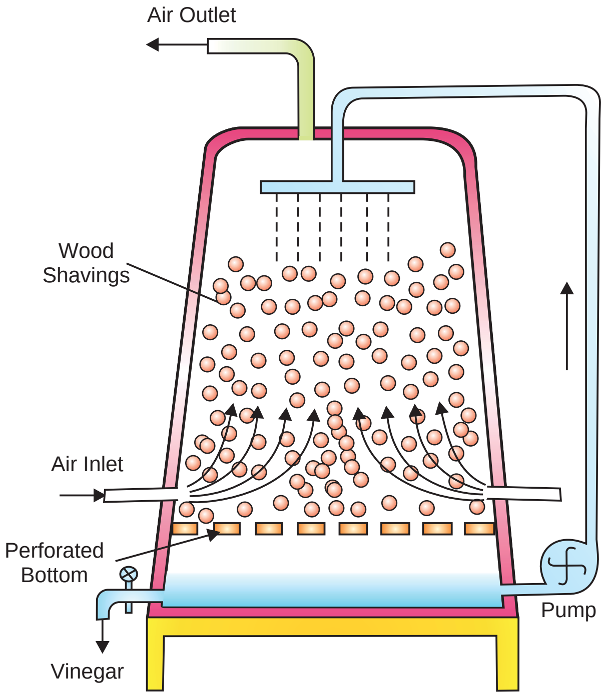


Figure 6.4 Industrial preparation of acetic acid.

6.1.5 Fatty Acids

Activity 6.6

Form a group and discuss the following question. After the discussion, share your idea with the rest of the class.

1. What are fatty acids and why are they named so?
2. Give some examples of fatty acids.

Fatty acids are a carboxylic acids with a long hydrocarbon chains. Fatty acids are found in all cells. The hydrocarbon chains of animal fatty acids are more saturated than those of vegetable origin. With only a few exceptions, the fatty acids are all straight-chain compounds. Most fatty acids contain an even number of carbon atoms.

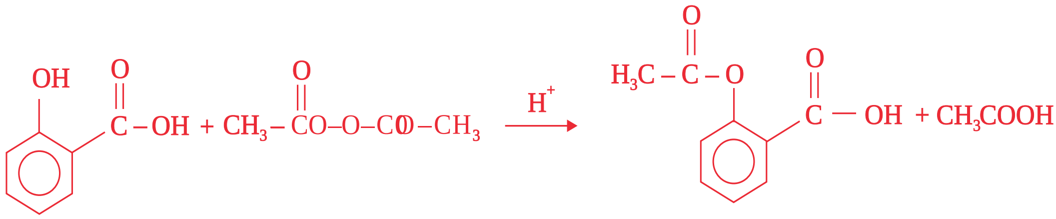
Fatty acids that do not contain carbon-carbon double bonds are termed as saturated fatty acids, and those that contain one or more double bonds are called unsaturated fatty acids. When there is only one double bond, it is usually between the ninth and tenth carbon atoms in the chain. Some common fatty acids present in different fats and oils are listed in Table 6.6.

Table 6.6 Examples of naturally occurring saturated fatty acids

Name	Formula
Lauric acid	$CH_3(CH_2)_{10}COOH$
Myristic acid	$CH_3(CH_2)_{12}COOH$
Palmitic acid	$CH_3(CH_2)_{14}COOH$
Stearic acid	$CH_3(CH_2)_{16}COOH$
Arachidic acid	$CH_3(CH_2)_{18}COOH$

6.1.6 Uses of Carboxylic Acids

Acetic acid is used as a solvent and as a starting material in the preparation of acetates, acetic anhydride, etc. It is also used to prepare the vinyl acetate polymer which is used in paints and adhesives. Vinegar contains about 8-10 % acetic acid which is used in many food items. Aspirin, the common painkiller, is prepared by the reaction of salicylic acid (2-hydroxylbenzoic acid) with acetic anhydride.



Salicylic acid

Acetylsalicylic acid
(Aspirin)

Carboxylic acids are very important, industrially. Perhaps one of the most important industrial applications of long chain carboxylic acid is for making soaps, detergents, and shampoos. Carboxylic acids are also important in the manufacture of greases, crayons, and plastics.

They are used commerically as raw materials for the production of synthetic odors and flavors.

6.2 ESTERS

At the end of this section, you should be able to:

- list common sources of esters;
- write the general structural formula of esters;
- write the molecular formulas and names of some simple esters;
- describe the physical properties of esters;
- explain the chemical properties of esters;
- explain the general methods of preparation of esters; and
- describe some common uses of esters

6.2.1 Sources of Esters

Activity 6.7

Form a group and discuss the following:

Why do some fruits and flowers have pleasant odours?

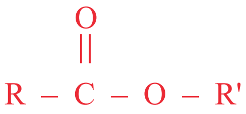
Share your ideas with the rest of the class.

Esters are among the most widely occurring compounds in nature. Many esters are pleasant-smelling substances and are responsible for the flavor and fragrance of many fruits for example, apples, pears, banana, pineapple, strawberry, etc. Oils, fats and waxes of plants or animal origin are all esters. Many esters are found in flowers also and form the part of essential oils obtained from flowers.

6.2.2 Structure and Nomenclature of Esters

Esters are derivatives of carboxylic acids in which the hydroxyl group of carboxylic acid has been replaced by an alkoxy group. Esters can also be formed by the reaction between acid anhydrides and phenols. In such cases, the hydroxyl group is replaced by an alkoxy group.

Esters can be represented by the general formula



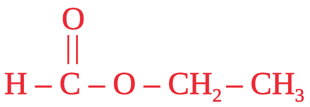
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$$

where R = hydrogen, alkyl or an aryl group and R′ = alkyl or an aryl group.

Esters are named by the common system as well as by IUPAC system. In both the cases, the name consists of two parts. The first part is named on the basis of the portion coming from alcohol and the second part of the name is based on the portion from acid. Therefore, it is necessary to identify first the portions coming from alcohol and carboxylic acid.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-O-R' \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'$$

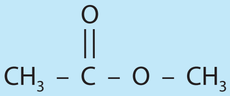
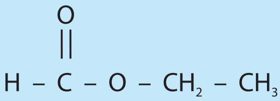
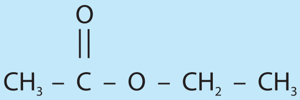
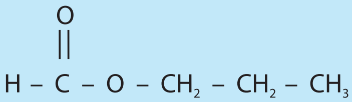
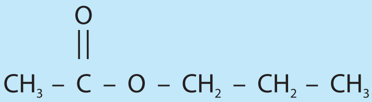
The above reaction shows that the portion coming from alcohol is attached to the oxygen as alkyl group, and the acid portion is attached to the oxygen through carbonyl group. While writing the name of an ester, first the name of alkyl group is written first followed by the name of the acid by replacing -ic acid with -ate. When we use the common name of carboxylic acid, the name of the ester is a common name, and when IUPAC name of the acid is used, we get IUPAC name for ester. For illustration, consider the ester formed from ethyl alcohol and methanoic acid.



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3$$

The common name for this ester is ethyl formate, and the IUPAC name is ethyl methanoate. The formulae and names of some esters are listed in Table 6.7.

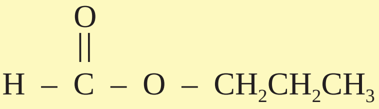
Table 6.7 Names and formulae of some common esters

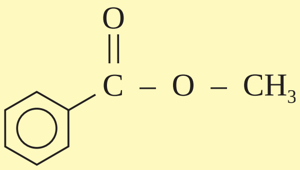
Molecular Formula	Structural Formula	Common Name	IUPAC Name
$C_3O_2H_6$	 $CH_3-\overset{\overset{O}{\parallel}}{C}-O-CH_3$	Methyl acetate	Methyl ethanoate
$C_3O_2H_6$	 $H-\overset{\overset{O}{\parallel}}{C}-O-CH_2-CH_3$	Ethyl formate	Ethyl methanoate
$C_4O_2H_8$	 $CH_3-\overset{\overset{O}{\parallel}}{C}-O-CH_2-CH_3$	Ethyl acetate	Ethyl ethanoate
$C_4O_2H_8$	 $H-\overset{\overset{O}{\parallel}}{C}-O-CH_2-CH_2-CH_3$	Propyl formate	Propyl methanoate
$C_5O_2H_{10}$	 $CH_3-\overset{\overset{O}{\parallel}}{C}-O-CH_2-CH_2-CH_3$	Propyl acetate	Propyl ethanoate

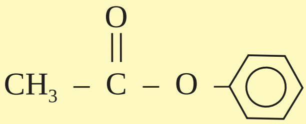
Note that in the given Table 6.7 molecular formula can represent more than one structure. For example, methyl ethanoate and ethyl methanoate have the same molecular formula, $C_3O_2H_6$. Similarly, ethyl ethanoate and propyl methanoate have the same molecular formula.

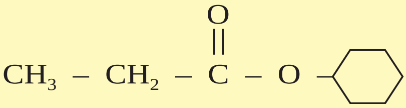
Exercise 6.5

1. Name the following esters.

a 
$H-\overset{\overset{O}{\parallel}}{C}-O-CH_2CH_2CH_3$

c 

b 

d 

2. Write the structure of the following esters:
   a Isopropyl methanoate
   b Ethyl propanoate

6.2.3 Physical Properties of Esters

Activity 6.8

Form a group and discuss the following questions. After the discussion, share your ideas with the rest of the class.

1. Do you expect esters to have lower or higher boiling points compared to carboxylic acids of comparable molecular mass?
2. Do you expect esters to have lower or higher boiling points compared to alcohols of comparable molecular mass?

i) Odour

In sharp contrast to the disagreeable odours of carboxylic acids, esters have pleasant odour. The odour of many fruits and flowers result from mixtures of carboxylic esters, and many of them are used in perfumes and food flavoring.

ii) Boiling points

The boiling points of esters increase with increasing molecular mass. Branched-chain esters have lower boiling points than their straight-chain isomers. Esters have lower boiling points than carboxylic acids and alcohols of comparable molecular mass. This is because ester molecules cannot form hydrogen bonds with each other.

iii) Solubility

Esters of low molecular mass are fairly soluble in water. Since carboxylic esters can form hydrogen bonding with water (Figure 6.5), it is not surprising that their solubility in water is about the same as that of carboxylic acids of the same molecular mass. The solubility of esters in water decreases with increasing molecular mass. All esters are soluble in organic solvents.

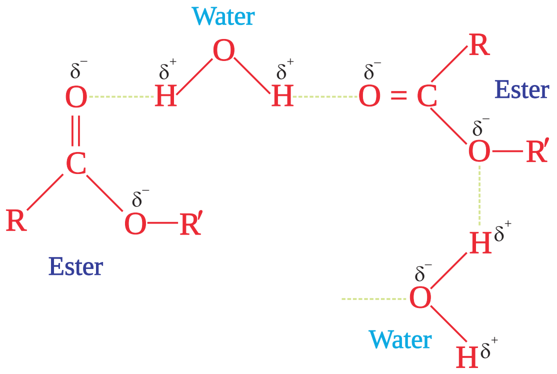


Figure 6.5 Hydrogen bonding between ester and water molecule.

6.2.4 Chemical Properties of esters

Activity 6.9

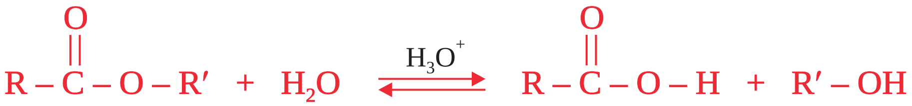
Form a group and discuss the following questions. After the discussion, share your ideas with the rest of the class.

1. What would happen when esters are treated with water?
2. Recall the reactants that form esters. What was the by-product of the condensation reaction?

i) Hydrolysis

One of the most important reactions of esters is their hydrolysis, which yields corresponding carboxylic acids and alcohols. The hydrolysis reaction is speeded up in presence of a mineral acid which act as catalyst in this reaction.

The general reaction for acid-catalyzed hydrolysis of esters can be written as:

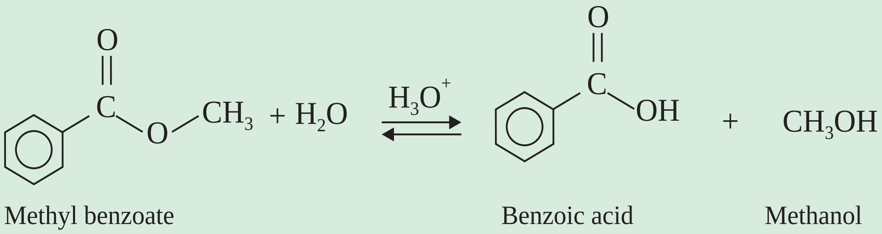


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O \overset{H_3O^+}{\rightleftharpoons} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + R'-OH$$

Example 6.11

Write an equation showing the acid-catalyzed hydrolysis of methyl benzoate.

Solution:



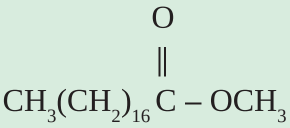
Esters also undergo base-catalyzed hydrolysis to give salts of carboxylic acids and alcohols. Base-catalyzed ester hydrolysis is called saponification. Sodium hydroxide or potassium hydroxide are the bases generally used for hydrolysis. For synthetic purpose, base catalysis is often preferred, because the reaction is not reversible.

The general reaction for base-catalyzed hydrolysis of esters:

$$R-\overset{\overset{O}{\|}}{C}-O-R' + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^{-}Na^{+} + R'-OH$$

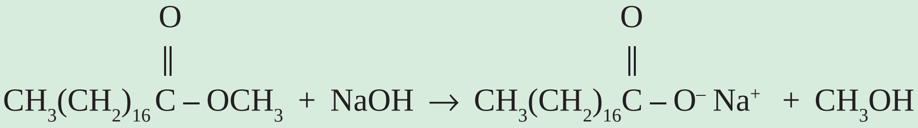
Example 6.12

Write an equation showing the base-catalyzed hydrolysis of methyl octadecanoate.



$$CH_3(CH_2)_{16}\overset{\overset{O}{\|}}{C}-OCH_3$$

Solution:

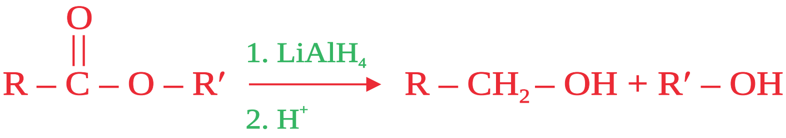


$$CH_3(CH_2)_{16}\overset{\overset{O}{\|}}{C}-OCH_3 + NaOH \rightarrow CH_3(CH_2)_{16}\overset{\overset{O}{\|}}{C}-O^{-}Na^{+} + CH_3OH$$

In biological systems, many ester hydrolysis reactions take place, for example, in the digestion of fats. These reactions occur under very mild conditions, and in the presence of certain biological catalysts known as enzymes.

i) Reduction

Esters are reduced to primary alcohols by special reducing agents like lithium aluminium hydride, $LiAlH_4$. The general reaction for reduction of esters is given by:

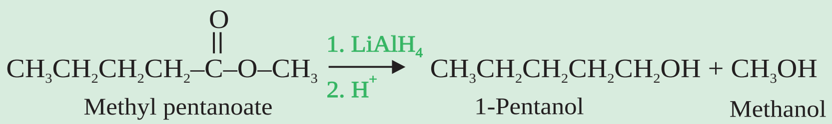


$$R-\overset{\overset{O}{\|}}{C}-O-R' \xrightarrow[2.\ H^{+}]{1.\ LiAlH_4} R-CH_2-OH + R'-OH$$

Example 6.13

Write an equation showing the reduction of methyl pentanoate.

Solution:

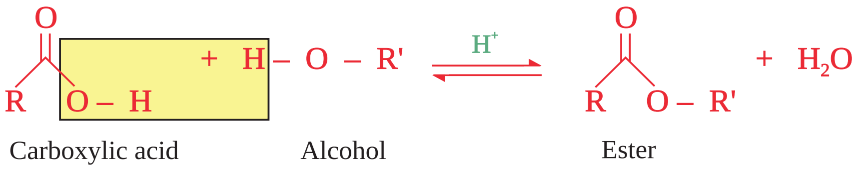


$$CH_3CH_2CH_2CH_2-\overset{\overset{O}{||}}{C}-O-CH_3 \xrightarrow[2.\ H^+]{1.\ LiAlH_4} CH_3CH_2CH_2CH_2CH_2OH + CH_3OH$$

Methyl pentanoate 1-Pentanol Methanol

6.2.5 Preparation of Esters

Esters can be synthesized by heating a mixture of a carboxylic acid and an alcohol in the presence of an acid catalyst such as H_2SO_4. This reaction is called esterification and is a common method for the preparation of esters.

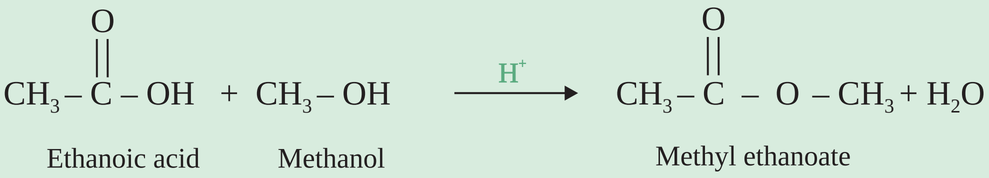


In this condensation reaction, the hydroxyl group (–OH) from the acid and a hydrogen atom (–H) from the alcohol are eliminated in the form of water, as indicated by the dotted rectangle in the above reaction.

Example 6.14

Write an equation showing the preparation of methyl ethanoate from methanol and ethanoic acid.

Solution:



$$CH_3-\overset{\overset{O}{||}}{C}-OH + CH_3-OH \xrightarrow{H^+} CH_3-\overset{\overset{O}{||}}{C}-O-CH_3 + H_2O$$

Ethanoic acid Methanol Methyl ethanoate

Exercise 6.6

Write the reactions for the preparation of each of the following esters using appropriate acids and alcohols:

a Ethyl acetate
b Ethyl butanoate
c Methyl benzoate
d Phenyl ethanoate

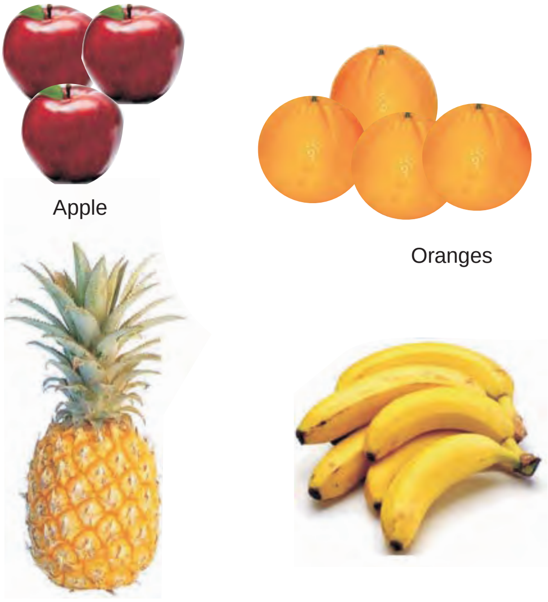
6.2.6 Uses

Esters have numerous uses as solvents, medicines, clothing (*e.g*. polysters), fragrances in perfumes, and plasticizers (e.g. octyl phthalate).

Most esters of small acids and alcohols are non-corrosive, non-toxic liquids with good properties for use as solvents. Esters are used as solvents for oils and fats, nail polishes, varnishes, paints, gums and resins. Because of their pleasant fruity smells, esters are used in making artificial flavours and perfumes. Table 6.8 depicts same common fruits and the esters responsible for their flabours (see also Figure 6.6).

Table 6.8 Some common fruits and the esters responsible for their flavour

Fruit	Ester present
Apple	Ethyl isovalerate
Pineapple	Methyl butanoate and Ethyl butanoate
Banana	Isopentyl acetate
Orange	Octyl acetate


Apple

Oranges

Pineapple

Bananas

Figure 6.6 Some fruits containing ester.

6.3 FATS AND OILS

At the end of this section, you should be able to:

- define fats and oils ;
- write the general structural formula for fats and oils;

- present the structures of some common trigycerides;
- describe physical properties of fats and oils;
- explain the hardening of oils (process of converting oils to hard fats);
- explain rancidity;
- define soap and detergent;
- explain saponification;
- prepare soap; and
- explain the cleaning action of soaps.

6.3.1 Source and Structure of Fats and Oils

Activity 6.10

Form a group and perform the following activity:

Collect samples of butter, lard, tallow, peanut oil, soyabean oil and olive oil. Classify them according to vegetable or animal origin and according to their physical state. Do you find any relation between their source and the physical state?

Share your ideas with the rest of the class.

Fats and oils belong to a class of biomolecules called lipids. They are triesters of glycerol which are collectivity known as triglycerides or triacylglycerols.

The distinction between a fat and an oil depends on their physical states. If the substance is solid or semisolid at ordinary temperature, it is termed as a fat and if it is fluid, it is called an oil.

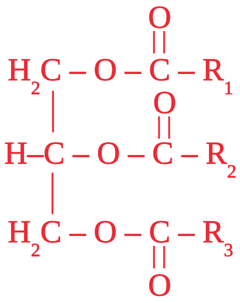
Fats and oils are widely found in nature especially in living things. Animal fats and oils are derived both from terrestrial (land) and marine (water) animals. Marine fats include liver oils, blubber oils, and fish oils.

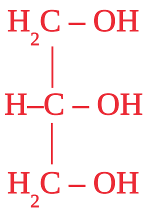
Vegetable fats and oils are found in greatest abundance in fruits and seeds. While fats and oils occur in the roots, stalks, branches and leaves of plants.

Structure of Fats and Oils

Fats and oils are triesters. Variation in the structure of fats and oils occur in the fatty acid portion of the triglyceride (or triacylglycerol).

Fats and oils are represented by the following general structural formula:

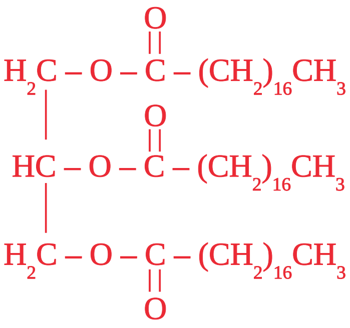

A triglyceride (triacylglycerol)

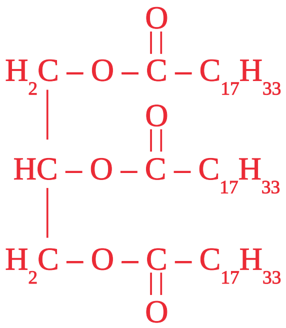

Glycerol

Where R_1, R_2 and R_3 may be the same or different hydrocarbon groups.

Fats are esters of glycerol and mostly saturated fatty acids and oils are liquid esters primarily derived from unsaturated fatty acids and glycerol. The acid part of fats and oils almost always contain on even number of carbon atoms.

The structures of some common triglycerides are shown below:


Glyceryl tristearate (stearin) fat


Glyceryl trioleate (olein) oil

Exercise 6.7

Write the structure of:

(*a*) Glyceryl trimyristate

(*b*) Glyceryl palmitooleostreate

Some of the commercialy available vegetable oils are shown in Figure 6.7.

Figure 6.7 Some vegetable oils.

6.3.2 Physical Properties of Fats and Oils

Activity 6.11

From a group and compare vegetable oils with mineral oils. Do they behave in similiar fashion? Explain.

Share your ideas with the rest of the class.

The common physical properties of fats and oils are that; they are greasy to the touch, and have lubricating properties; they are not readily volatile; and may be burned without leaving any residue, that is, ash.

Fats like butter, lard and tallow are solids at room temperature. On the other hand, oils are mainly obtained from plants, e.g., corn oil, peanut oil, cotton seed oil, olive oil and soyabean oil which are liquids at room temperature. All oils and fats are colourless, odourless and neutral substances in pure state. They are lighter than water and immiscible with it. They are soluble in organic solvents *e.g.* benzene, ether and chloroform etc.

6.3.3 Hardening of Oils

Activity 6.12

Form a group and classify the given fatty acids as saturated or unsaturated fatty acids:

Myristic acid, oleic acid, linolic acid, lauric acid, palmitic acid, linolenic acid and stearic acid.

Saturated fatty acids	Unsaturated fatty acids
____________________	____________________
____________________	____________________
____________________	____________________

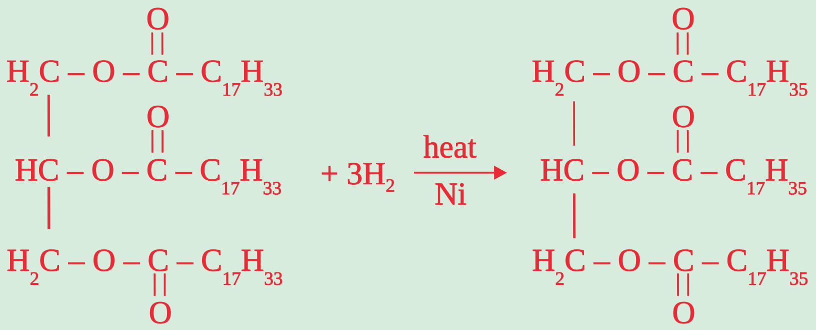
Can you suggest a method of converting unsaturated fatty acids to saturated fatty acids.

Present your findings to the class.

Oils can be converted to fats by addition of hydrogen (hydrogenation) at high pressure in presence of nickel or palladium as catalyst. This process of converting oils to hard fats is known as hardening of oils. This reaction is used in the preparation of margarine.

Example 6.15

A glyceryl tristearate (found in animal fat) can be prepared by hydrogenation of glyoryl trioleate (oil found in olive oil and whole oil) is shown in the equation below



Glyceryl trioleate

Glyceryl tristearate

Exercise 6.8

Write the equation for the hydrogenation of:

(*a*) Glyceryl palmitooleostreate, and

(*b*) Glyceryl trimyristate

6.3.4 Rancidity

Activity 6.13

Form a group and perform the following activity:

Obtain two packets of fried potato chips from the market. Open one packet and smell it. Now place half the contents in a close tight container and other half in an open container. Let the second packet be kept as such. After 15 days, smell the chips kept in the open container, closed container and sealed packet. Record your observations and find out what is the best method to keep such items.

Share your findings with the class.

Fats and oils are quite reactive substances. When stored for any considerable length of time, especially when the temperature is high and the air has free access to them, they deteriorate and spoil. Among the various fats, spoilage takes the form of rancidity.

Fats and oils develop an unpleasant odour due to rancidity. It is caused mainly due to the hydrolysis of ester linkage and oxidation across the double bonds. In this respect, different fats differ markedly. Some spoil very much more rapidly than others. The fat acquires a peculiarly disagreeable odor and flavor.

The rancidity of a given fat is not necessarily the result of long storage under unfavorable conditions. The fat may have been spoiled and rancid from the moment of its production. This will inevitably be true when the materials from which it was produced have undergone decomposition. In other words, to obtain a sound and sweet fat, the raw material must be sound and sweet; it must be processed speedily before it gets time to decompose; and this must be done under clean and sanitary conditions. The fat thus obtained must be stored under favorable conditions and its consumption should not be delayed.

6.3.5 Soaps and Detergents

Activity 6.14

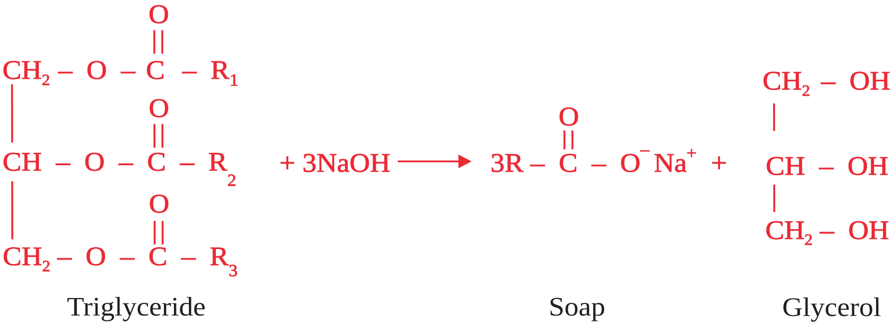
Form a group and collect the information regarding the substances which were used for cleaning before the discovery of soaps. Share the information with the class.

The commercialy available soaps are shown in Figure 6.8.

Figure 6.8 Some commercially available soaps.

i) *Soaps*

Soaps are sodium or potassium salts of long chain fatty acids. These are generally obtained by alkaline hydrolysis of oils and fats. This process is called saponification. A general reaction can be written as follows:



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R_1 \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R_2 \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R_3 \end{array} + 3NaOH \longrightarrow 3R-\overset{O}{\overset{\|}{C}}-O^{-}Na^{+} + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Although chemically all soaps are salts of fatty acids but many variations are created when used for specific purposes, for example colour and perfumes are added when used as toilet soap.

Transparent soaps are prepared by first dissolving in alcohol and then evaporating the excess alcohol. Floating soaps are prepared by beating air before it hardens during manufacture. Certain antibacterial substance are also added for making medicinal soaps. Potassium salts of fatty acids form soft soaps and are used as baby soaps.

ii) Detergents

Detergents are synthetic substances which are used as substitutes to soaps. Although synthetic detergents vary considerably in their chemical structure, the molecules of all of them have one common feature which they share with ordinary soaps. They are amphipathic, have a large non-polar hydrocarbon end that is oil-soluble and a polar end that is water-soluble.

The C_{12}-C_{18} alcohols are converted into the salts of alkyl hydrogen sulphate by treatment with H_2SO_4. The resulting alkyl sulphates, when treated with NaOH, produce a detergent, sodium alkyl sulphate.

For example, sodium lauryl sulphate, a very common detergent is obtained from lauryl alcohol as shown in the following reaction.

$$\underset{\text{Lauryl alcohol}}{CH_3\,(CH_2)_{10}-CH_2-OH} + H_2SO_4 \longrightarrow \underset{\text{Lauryl hydrogen sulphate}}{CH_3-(CH_2)_{10}-CH_2-OSO_3H} \xrightarrow{\text{NaOH}} \underset{\text{Sodium lauryl sulphate}}{CH_3(CH_2)_{10}-CH_2-OSO_3^-\ Na^+}$$

Detergents act in essentially the same way as soap does. However, they have certain advantages over soap. For example, the sulphates retain their efficiency in hard water, since the corresponding calcium or magnesium salts are soluble. Hence detergents can be used in hard water. Detergents are neutral whereas soaps are basic. But, detergents are not without drawbacks. For example, some are not biodegradable, which makes them environmentally non-friendly. The new detergents are better in being more biodegradable than the older generation.

iii) Saponification (Soap-making)

Soap-making (saponification) is one of the oldest chemical technologies. Man first boiled goat tallow and wood ash to give a lathering and cleansing product. The goat tallow contained the needed ester, and the wood ash the necessary alkali. Chemicals with the same reactive groups are the main raw materials still used in traditional and modern soap manufacture. Remember that saponification is the chemical process of breaking down an ester in presence of alkali to form soap.

Experiment 6.2

Laboratory Preparation of Soap

Objective: To prepare soap in the laboratory by the alkaline hydrolysis of fats and oils.

Apparatus: Water-cooled condenser, 100 mL flask, Bunsen burner, Buchner funnel ring stand, clamp, boiling chips and 400 mL beaker.

Chemicals: Animal fat (tallow) or vegetable oil, NaOH, ethanol and table salt.

***Procedure*:**

1. Set up a reflux apparatus as shown in Figure 6.9.
2. Place 3 mL of vegetable oil or 3 g of animal fat (tallow) in the 250 mL distillation flask.
3. Add about 15 mL of 20 % sodium hydroxide solution.
4. Add a few boiling chips and connect the flask to the condenser and gently reflux the mixture over a small flame. Saponification is complete when a homogeneous solution is obtained (in 30 - 45 minutes).
5. While the saponification is in progress, prepare a concentrated salt solution by dissolving 50 g of NaCl in a 150 mL of water in a 400 mL beaker.
6. When saponification is complete, extinguish the flame and pour the mixture quickly into the saturated NaCl solution (brine).
7. Stir the mixture thoroughly for several minutes.
8. Collect the precipitated soap on a Buchner funnel.
9. Wash the soap twice with 10 mL of ice-cold distilled water.Wait until it dries.

Observations and Analysis :

1. What happens to the animal fat (tallow) or vegetable oil in this reaction?
2. What is the role of sodium hydroxide?
3. Write the chemical reaction for this reaction.
4. What do you conclude from this activity?

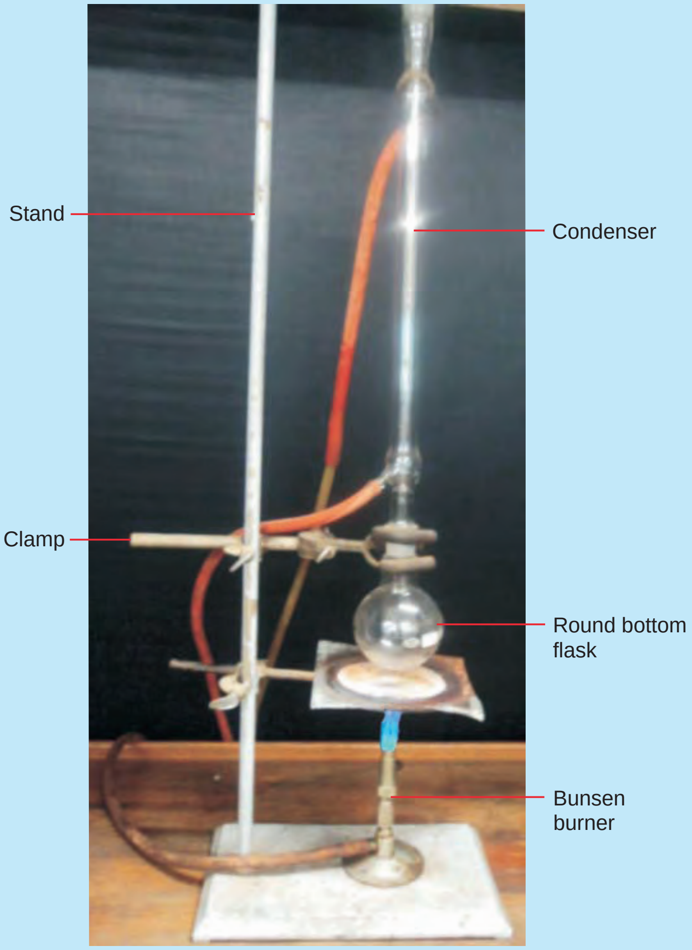
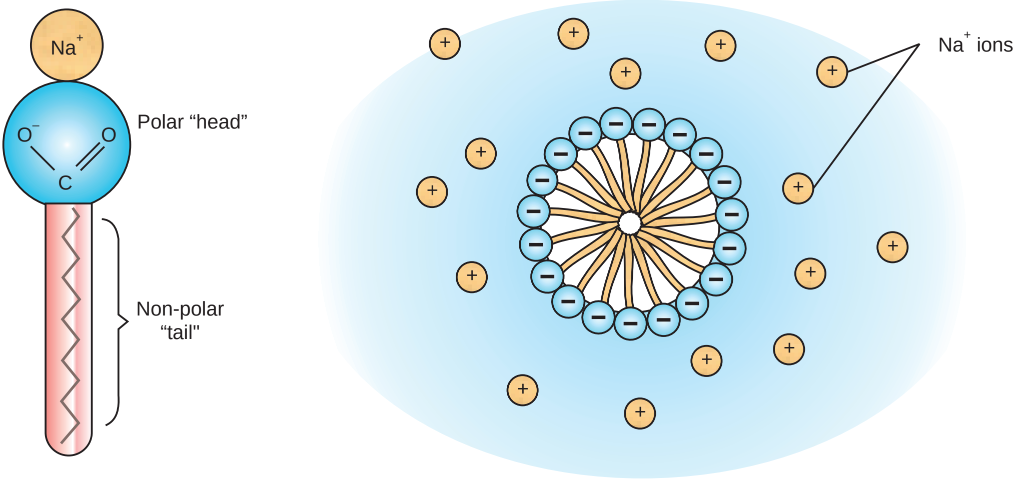


Figure 6.9 Laboratory set up for preparation of soap.

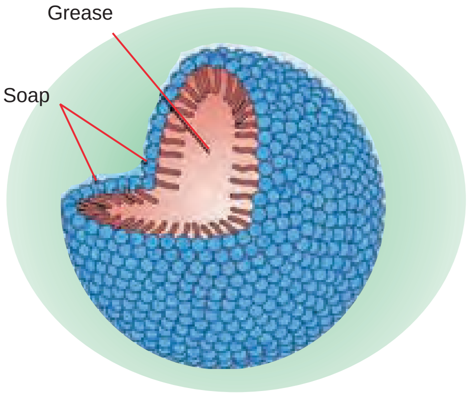
iv) *Cleaning Action of Soap*

Molecules of soap have two dissimilar ends. At one end is long carbon chain which is hydrophobic or water repellant. The other end has carboxylate ion which is water soluble end. So soap molecules have both polar and non-polar ends and, in addition, are big enough for each end to display its own solubility behaviour. Such molecules are called amphipathic. When they are dissolved in water, each non-polar end seeks a non-polar environment in line with rule of "like dissolves like". Therefore, many nonpolar ends clump together to form the micelles as shown in Figure 6.10.



(a) A soap

(b) Cross section of a soap micelle in water



(c) Soap micelle with "dissolved" grease

Figure 6.10 Soap molecules form micelles when "dissolved" in water.

When a cloth with spot of oil and dirt is soaked into the soap solution, the tiny droplets of oil are dissolved by the hydrocarbon end in the middle of the micelle. Due to the outwardly projected polar ends, these micelles dissolve in water and are washed away. In this way soaps act as cleaning agents.

Exercise 6.9

What saponification products would be obtained when mixing the following oils with NaOH?

1. Glyceryl trimyristate
2. Glyceryl palmitooleostearate.

Unit Summary

- *Carboxylic acids are compounds with a –COOH functional group.*
- *Because of the –COOH functional group, carboxylic acids are polar compounds and can form hydrogen bondings with water and among themselves.*
- *The common names of carboxylic acids are based on their origins in nature whereas their IUPAC names are created by replacing the ending "e" of the corresponding alkane, or alkyne by "oic acid."*
- *Carboxylic acids are generally prepared by the oxidation of corresponding primary alcohols.*
- *Esters are mildly polar compounds that are widely distributed in nature.*
- *Esters are named according to both the common name system and the IUPAC system.*
- *In a laboratory, esters can be prepared from a reaction between a carboxylic acid and an alcohol. The process requires an acid catalyst and heating.*
- *Fats and oils are esters of long-chain carboxylic acid with glycerol.*
- *Soaps are sodium or potassium salts of long-chain carboxylic acids. They can be prepared by the saponification of fats or oils, using a base (NaOH or KOH).*
- *One of the main difference between soaps and detergents is that the detergents can be used in hard water, whereas soaps form scum in hard water.*

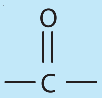
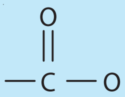
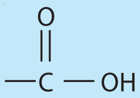
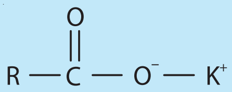
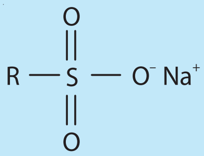
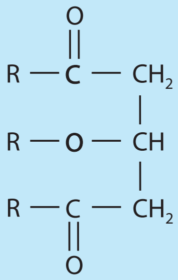
Check List

Key terms of the unit

- *Carboxyl group*
- *Carboxylic acid*
- *Detergents*
- *Ester*
- *Esterification*
- *Fat*
- *Hardening of oils*
- *Lipid*
- *Oil*
- *Rancidity*
- *Saponification*
- *Soaps*
- *Triglycerides*

REVIEW EXERCISE

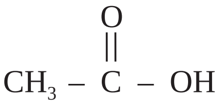
Match the names of the functional group in cloumn A with the structure in column B.

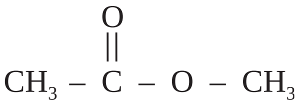
Names of the functional groups A	Structures B
(i) Carboxyl group	a  $-\overset{\overset{O}{\|}}{C}-$
(ii) Carbonyl group	b  $-\overset{\overset{O}{\|}}{C}-O$
(iii) Ester group	c  $-\overset{\overset{O}{\|}}{C}-OH$
(iv) Fats and Oils	d  $R-\overset{\overset{O}{\|}}{C}-O^{-}-K^{+}$
(v) Soaps	e  $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{-}Na^{+}$
(vi) Detergents	f 

Part I : Multiple Choice Questions

1. Which of the following compounds reacts with sodium bicarbonate?

   a $CH_3 - CH_2 - OH$

   b  $CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - OH$

   c  $CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - O - CH_3$

   d $CH_3 - CH_2 - CH_3$

2. The compound ‘A’ when treated with methyl alcohol and few drops of H_2SO_4 gave fruity smell. The compound ‘A’ can be:

   a toluene

   b ethanol

   c propanoic acid

   d methyl ethanoate

3. The reaction between alcohol and carboxylic acids is called:

   a esterification

   b saponification

   c hydrolysis

   d dehydration

4. Conversion of ethanol into ethanoic acid is an example of:

   a reduction

   b oxidation

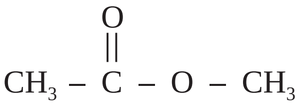
   c addition

   d hydration

5. When ‘tella’ is kept for some time, it becomes sour due to the formation of:

   a $CH_3 - CH_2 - OH$

   b HCOOH

   c  $CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - O - CH_3$

   d CH_3COOH

6. Toluene can be converted into benzoic acid by its reaction with:

   a sodium metal

   b potassium hydroxide

   c potassium permanganate

   d carbon dioxide

7. Carboxylic acids of low molecular mass are soluble in water due to:

   a hydrogen bonding

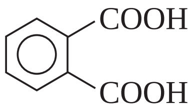
   b dimer formation

   c dissociation into ions

   d hydrolysis

8. Hydrolysis reaction of fats by sodium hydroxide is known as:
   - a acetylation
   - b carboxylation
   - c saponification
   - d esterification
9. What happens when an ester is treated with $LiAlH_4$?
   - a One unit of alcohol and one unit of acid is formed.
   - b Two units of alcohol are formed.
   - c Two units of carboxylic acid are formed.
   - d No reaction occurs.
10. Detergents are better than soaps because they:
    - a are naturally available.
    - b are biodegradable.
    - c can be used in hard water.
    - d All of these.

Part II : Answer the following questions

11. Draw the structures for the following compounds:
    - a 3-bromobutanoic acid
    - b 2-hydroxy-2-methylpropanoic acid
    - c 2-butanoic acid
    - d benzoic acid
12. Name the following compounds:
    - a HCOOH
    - b $(CH_3)_2CHCOOH$
    - c $HOOC\text{-}CH_2CH_2\text{-}COOH$
    - d 

    - e $CH_3(CH_2)_{14}COOH$
13. Draw the structures of the following esters:
    - a iso-butyl acetate
    - b ethyl formate
    - c iso-pentyl acetate
    - d benzyl benzoate
    - e octyl ethanoate

14. Name the alcohol and the acid from which each of these esters is produced.

    a isopentyl acetate
    b benzyl benzoate
    c octyl ethanoate
    d isobutyl acetate
    e ethyl formate

15. Complete the following reaction using structural formulas:

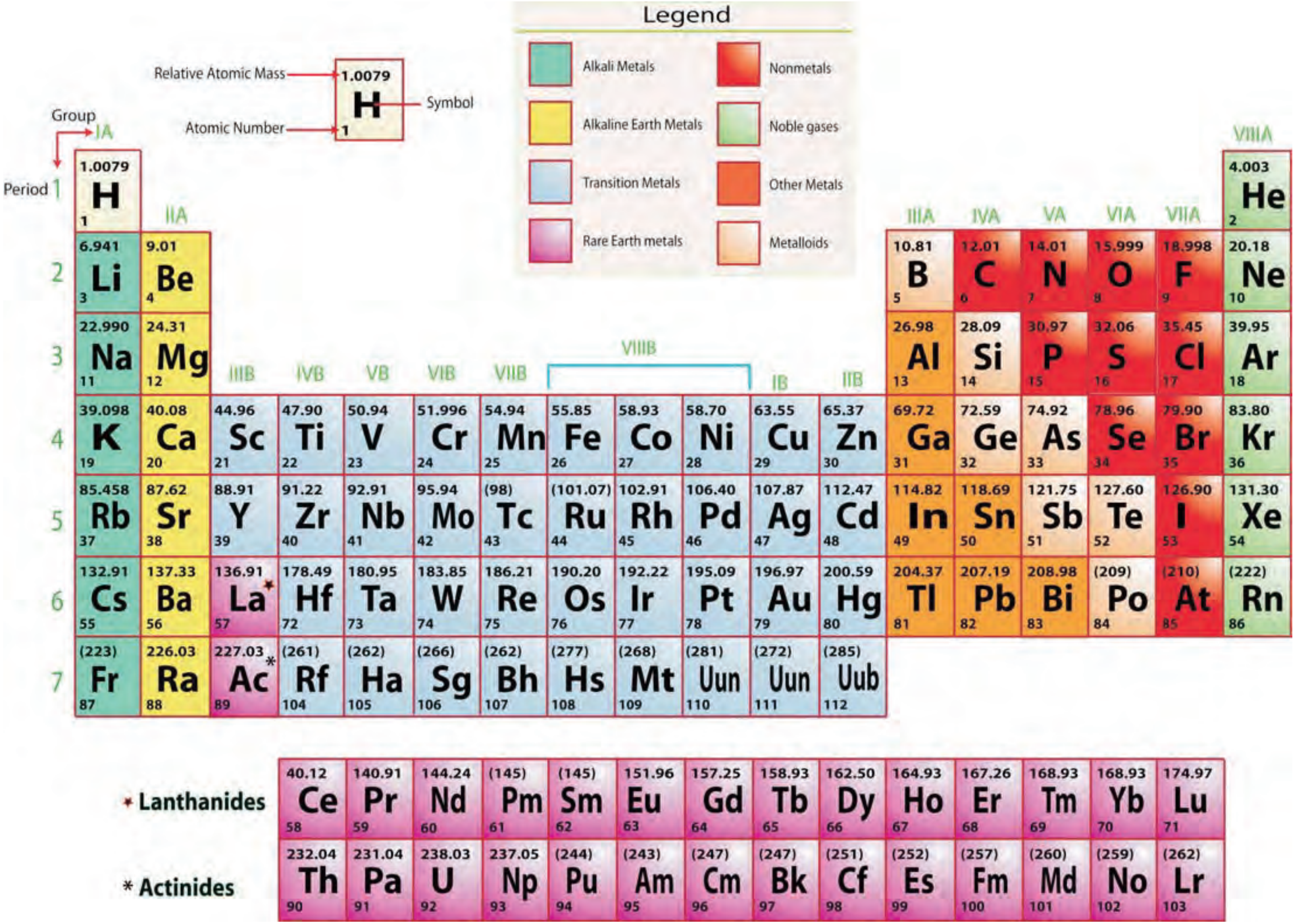
    Glyceryl tristearate + Potassium hydroxide →

16. Define the following giving suitable examples:

    a Hydrolysis
    b Saponification
    c Esterification
    d Hydrogenation
    e Lipids
    f Triglycerides
    g Rancidity
    h Hardening of oils

17. How will you carry out the following conversions?

    a Propan-1-ol into propanoic acid.
    b Propyl propanoate into propan-1-ol.



Legend

- 🟩 Alkali Metals
- 🟨 Alkaline Earth Metals
- 🟦 Transition Metals
- 🟪 Rare Earth metals
- 🟥 Nonmetals
- 🟩 Noble gases
- 🟧 Other Metals
- 🟧 Metalloids

Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.0079 H 1																	4.003 He 2
2	6.941 Li 3	9.01 Be 4											10.81 B 5	12.01 C 6	14.01 N 7	15.999 O 8	18.998 F 9	20.18 Ne 10
3	22.990 Na 11	24.31 Mg 12											26.98 Al 13	28.09 Si 14	30.97 P 15	32.06 S 16	35.45 Cl 17	39.95 Ar 18
4	39.098 K 19	40.08 Ca 20	44.96 Sc 21	47.90 Ti 22	50.94 V 23	51.996 Cr 24	54.94 Mn 25	55.85 Fe 26	58.93 Co 27	58.70 Ni 28	63.55 Cu 29	65.37 Zn 30	69.72 Ga 31	72.59 Ge 32	74.92 As 33	78.96 Se 34	79.90 Br 35	83.80 Kr 36
5	85.458 Rb 37	87.62 Sr 38	88.91 Y 39	91.22 Zr 40	92.91 Nb 41	95.94 Mo 42	(98) Tc 43	(101.07) Ru 44	102.91 Rh 45	106.40 Pd 46	107.87 Ag 47	112.47 Cd 48	114.82 In 49	118.69 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.30 Xe 54
6	132.91 Cs 55	137.33 Ba 56	136.91 La* 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.20 Os 76	192.22 Ir 77	195.09 Pt 78	196.97 Au 79	200.59 Hg 80	204.37 Tl 81	207.19 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	(223) Fr 87	226.03 Ra 88	227.03 Ac* 89	(261) Rf 104	(262) Ha 105	(266) Sg 106	(262) Bh 107	(277) Hs 108	(268) Mt 109	(281) Uun 110	(272) Uun 111	(285) Uub 112						

* Lanthanides	40.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	(145) Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	168.93 Yb 70	174.97 Lu 71
* Actinides	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(260) Md 101	(259) No 102	(262) Lr 103